Desymmetrization of 4-Hydroxy-2,5-cyclohexadienones by Radical Cyclization: Synthesis of Optically Pure γ-Lactones

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Supplementary Information

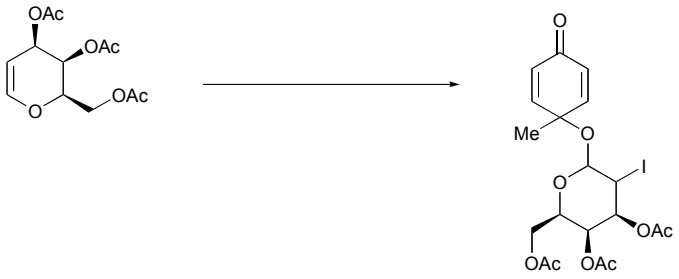
4-Hydroxy-4-methylcyclohexa-2,5-dienone (2).[4]

2

A mixture of Oxone (28.4 g, 46.2 mmol) and $NaHCO_3$ (11.65 g, 138.7 mmol) was added over ca 3 min to a vigorously stirred solution of *p*-cresol (0.97 mL, 9.3 mmol) in MeCN (10 mL) and water (40 mL). The flask was immediately closed with a septum attached via a needle to an empty balloon to avoid loss of generated singlet oxygen. Vigorous stirring was continued until all the phenol had reacted (TLC control). The mixture was diluted with water (15 mL), solid $Na_2S_2O_3$ (14.6 g, 92.5 mmol) was added and stirring was continued for 1 h. The mixture was

then partitioned between EtOAc and water and the aqueous phase was extracted with EtOAc. The combined organic extracts were washed with brine, dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (2 x 18 cm), using 50% EtOAc-hexane, gave **2** (825 mg, 72%) as a pale yellow solid: mp 77-78 °C, FTIR (microscope, cast) 3410, 2978, 2925, 1674, 1640, 1373 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.49 (s, 3 H), 2.04 (s, 1 H), 6.15 (d, *J* = 10.2 Hz, 2 H), 6.88 (d, *J* = 10.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 26.6 (q), 67.1 (s), 127.1 (d), 151.9 (d), 185.2 (s).

1-Methyl-4-oxocyclohexa-2,5-dienyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-iodo-β-D-galacto-pyranoside (23).

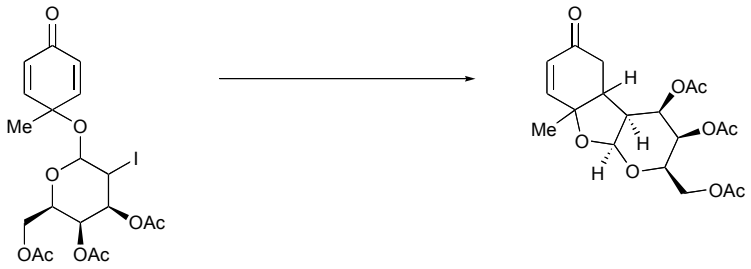


19 **23**

NIS (1.25 g, 5.58 mmol) was added to a stirred solution of D-galactal triacetate **19** (1.24 g, 4.56 mmol) in MeCN (20 mL) and the mixture was stirred at room temperature for 15 min. The cross conjugated enone **2** (461 mg, 3.72 mmol) was added and stirring was continued for 12 h. The mixture was diluted with Et_2O, washed with saturated aqueous $Na_2S_2O_3$ and brine, dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (2.5 x 18 cm), using 50% EtOAc-hexane, gave **23** (1.62 g, 68%) as an oil, which was a single isomer: $[\alpha]_D$ = 63.2 (*c* 3.09, $CHCl_3$); FTIR (microscope, cast) 2982, 1749, 1675, 1373, 1231 cm^{-1}; ^1H NMR

($CDCl_3$, 400 MHz) δ 1.50 (s, 3 H), 2.07 (s, 3 H), 2.08 (s, 3 H), 2.15 (s, 3 H), 4.11-4.13 (m, 1 H), 4.17-4.12 (m, 2 H), 4.41 (ddd, *J* = 7.6, 5.6, 2.0 Hz, 1 H), 4.97 (t, *J* = 4.5 Hz, 1 H), 5.22 (d, *J* = 1.6 Hz, 1 H), 5.37 (t, *J* = 2.8 Hz, 1 H), 6.20 (dd, *J* = 10.2, 1.9 Hz, 1 H), 6.34 (dd, *J* = 10.2, 1.9 Hz, 1 H), 6.74 (dd, *J* = 10.2, 3.1 Hz, 1 H), 6.89 (dd, *J* = 10.3, 3.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.5 (q), 20.7 (q), 20.8 (q), 21.6 (q), 26.1 (d), 61.8 (t), 65.1 (d), 65.2 (d), 67.2 (d), 73.6 (s), 99.1 (d), 128.1 (d), 130.7 (d), 148.4 (d), 150.2 (d), 169.3 (s), 170.0 (s), 170.1 (s), 184.5 (s); exact mass (electrospray) *m*/*z* calcd for $C_{19}H_{23}INaO_9$ (M + Na) 545.0279, found 545.0280.

Acetic Acid (3,4-Diacetoxy-3,4,4a,4b,5,6,8a,9a-octahydro-8a-methyl-6-oxo-2*H*-1,9-dioxafluoren-2-yl)methyl Ester (24).

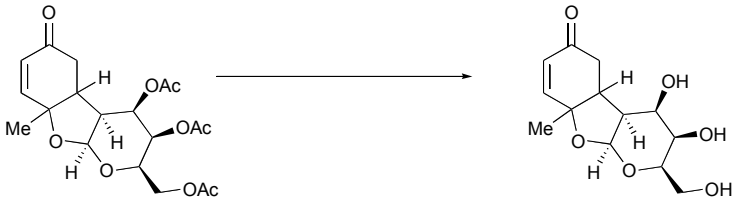


23 **24**

A solution of Bu_3SnH (0.22 mL, 0.85 mmol) and AIBN (11.6 mg, 0.071 mmol) in PhH (10 mL) was added over 1 h by syringe pump to a stirred and heated (85 °C) solution of **23** (369 mg, 0.707 mmol) in PhH (5 mL). Heating was continued for 12 h after the addition. Evaporation of the solvent and flash chromatography of the residue over KF-flash chromatography silica gel (10%w/w KF), using 50% EtOAc-hexane, gave the cyclized product **24** (209 mg, 75%) as an oil, which was a single isomer: $[\alpha]_D$ = 61.2 (*c* 2.16, $CHCl_3$); FTIR (microscope, cast) 2973, 1747, 1686, 1372, 1235 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.56 (s, 3

H), 2.01 (s, 6 H), 2.07 (s, 3 H), 2.21-2.24 (m, 1 H), 2.50-2.59 (m, 2 H), 2.62-2.70 (m, 1 H), 4.10 (dd, *J* = 11.4, 6.1 Hz, 1 H), 4.20 (dd, *J* = 11.4, 7.3 Hz, 1 H), 4.31 (ddd, *J* = 6.2, 6.2, 3.6 Hz, 1 H), 4.98 (dd, *J* = 7.6, 2.8 Hz, 1 H), 5.33 (d, *J* = 5.1 Hz, 1 H), 5.41 (dd, *J* = 3.5, 2.9 Hz, 1 H), 5.94 (dd, *J* = 10.3, 0.9 Hz, 1 H), 6.55 (dd, *J* = 10.3, 1.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.5 (q), 20.6 (q), 20.7 (q), 25.0 (q), 37.4 (t), 45.7 (d), 46.9 (d), 60.8 (t), 65.8 (d), 70.4 (d), 72.3 (d), 78.6 (s), 97.8 (d), 127.9 (d), 150.6 (d), 169.6 (s), 170.1 (s), 170.4 (s), 196.0 (s); exact mass (electrospray) *m*/*z* calcd for $C_{19}H_{24}NaO_9$ (M + Na) 419.1313, found 419.1315.

3,4,4a,4b,8a,9a-Hexahydro-3,4-dihydroxy-2-hydroxymethyl-8a-methyl-2*H*,5*H*-1,9-dioxafluoren-6-one (25).



24 **25**

MeONa (125 mg, 2.31 mmol) was added to a stirred solution of **24** (229 mg, 0.579 mmol) in dry MeOH (10 mL) and stirring was continued for 3 h. Amberlite (IR 120) was carefully added until the pH was 7, and the mixture was filtered. Evaporation of the filtrate gave crude **25** as white foam, which was used directly for the next step: FTIR (microscope, cast) 3395, 2934, 1713, 1675, 1377, 1236 cm^{-1}.

1-*O*-Acetyl-2,6-anhydro-5-deoxy-D-*arabino*-hex-5-enitol (pre-22).[17]

D-galactal **pre-22**

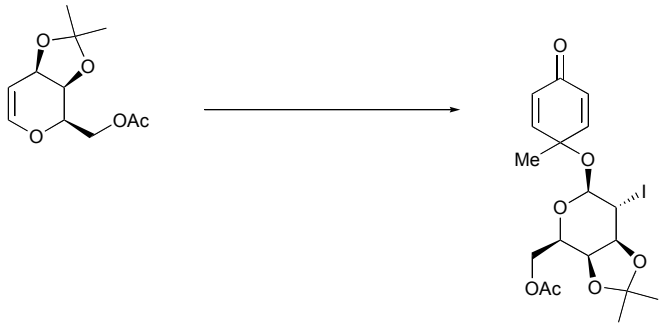
Vinyl acetate (25 mL) and powdered 4Å molecular sieves (4.0 g) were added to a stirred solution of D-galactal (2.0 g, 14 mmol) in water (2 mL). Lipase (from *Candida cylindracea*, LCC, 1.6 g) was added and the mixture was stirred for 45 min at room temperature. The mixture was then diluted with EtOAc, filtered and evaporated. Flash chromatography of the residue over silica gel (3 x 19 cm), using 50% EtOAc-hexane, gave **pre-22** (2.16 g, 84%) as a white foam: FTIR (microscope, cast) 3438, 2941, 1739, 1649, 1371, 1242 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.12 (s, 3 H), 2.34 (d, *J* = 8.6 Hz, 1 H), 2.44 (d, *J* = 6.9 Hz, 1 H), 3.92 (t, *J* = 5.2 Hz, 1 H), 4.10 (t, *J* = 5.9 Hz, 1 H), 4.33 (dd, *J* = 11.7, 7.1 Hz, 1 H), 4.43 (dd, *J* = 11.7, 5.4 Hz, 2 H), 4.74 (apparent dt, *J* = 6.2, 1.8, 1.8 Hz, 1 H), 6.40 (dd, *J* = 6.2, 1.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.9 (q), 63.4 (t), 63.9 (d), 65.2 (d), 74.5 (d), 103.0 (d), 144.5 (d), 171.2 (s); exact mass (electrospray) *m*/*z* calcd for $C_8H_{12}NaO_5$ (M + Na) 211.0577, found 211.0575.

1-*O*-Acetyl-2,6-anhydro-5-deoxy-3,4-*O*-(1-methylethylidene)-D-*arabino*-hex-5-enitol (22).

pre-22 **22**

2-Methoxypropene (0.46 mL, 4.8 mmol) and PPTS (252 mg, 1.00 mmol) were added to a stirred and cooled (0 °C) solution of **pre-22** (755 mg, 4.02 mmol) in dry CH_2Cl_2 (20 mL). After 30 min the ice bath was removed and stirring was continued for 4 h. Additional 2-methoxypropene (0.38 mL, 4.0 mmol) was added and stirring was continued for 12 h. Evaporation of the solvent and flash chromatography of the residue over silica gel (2 x 15 cm), using 10% EtOAc-hexane, gave **22** (764 mg, 84%) as an oil: $[\alpha]_D$ = 13.4 (*c* 5.19, $CHCl_3$); FTIR (microscope, cast) 2986, 2938, 1745, 1649, 1371, 1229 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.34 (s, 3 H), 1.45 (s, 3 H), 2.10 (s, 3 H), 4.10-4.25 (m, 1 H), 4.23-4.27 (m, 1 H), 4.30-4.42 (m, 2 H), 4.65 (dd, *J* = 6.2, 3.0 Hz, 1 H), 4.80 (ddd, *J* = 6.2, 2.9, 1.4 Hz, 1 H), 6.39 (d, *J* = 6.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.9 (q), 26.8 (q), 27.9 (q), 64.2 (t), 68.5 (d), 72.5 (d), 72.7 (d), 102.6 (d), 110.7 (s), 144.5 (d), 170.7 (s); exact mass (electrospray) *m/z* calcd for $C_{11}H_{16}NaO_5$ (M + Na) 251.0890, found 251.0894.

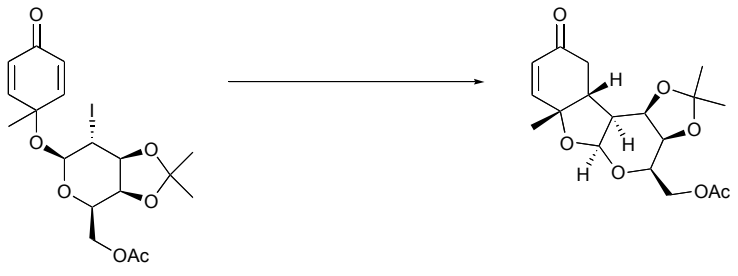
1-Methyl-4-oxocyclohexa-2,5-dienyl-6-*O*-Acetyl-2-deoxy-2-iodo-3,4-*O*-(1-methyl-ethylidene)-β-D-galactopyranoside (27).



22 **27**

NIS (403 mg, 1.79 mmol) was added to a stirred solution of D-galactal triacetate **22** (340 mg, 1.49 mmol) in MeCN (15 mL) and the mixture was stirred at room temperature for 20 min. The cross conjugated enone **2** (203 mg, 1.64 mmol) was added and stirring was continued for 12 h. The mixture was diluted with Et_2O, washed with saturated aqueous $Na_2S_2O_3$ and brine, dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (1.5 x 19 cm), using 30% EtOAc-hexane, gave **27** (494 mg, 69%) as an oil, which was a single isomer: $[\alpha]_D$ = 8.9 (*c* 4.57, $CHCl_3$); FTIR (microscope, cast) 2987, 2935, 1742, 1672, 1383, 1244 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.32 (s, 3 H), 1.48 (s, 3 H), 1.50 (s, 3 H), 2.06 (s, 3 H), 3.73 (t, *J* = 9.4 Hz, 1 H), 3.84-3.88 (m, 2 H), 4.21-4.29 (m, 3 H), 4.46 (dd, *J* = 8.8, 5.0 Hz, 1 H), 6.08 (dd, *J* = 10.2, 2.0 Hz, 1 H), 6.30 (dd, *J* = 10.1, 2.5 Hz, 1 H), 6.95-7.04 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.7 (q), 25.9 (q), 26.0 (d), 28.2 (q), 32.6 (q), 63.3 (t), 71.6 (d), 73.3 (d), 74.1 (s), 82.2 (d), 98.6 (d), 110.6 (s), 127.0 (d), 130.3 (d), 149.4 (d), 151.7 (d), 170.5 (s), 185.1 (s); exact mass (electrospray) *m*/*z* calcd for $C_{18}H_{23}INaO_7$ (M + Na) 501.0381, found 501.0386.

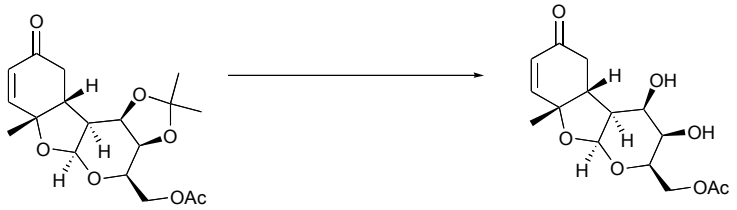
Acetic Acid (3a*R*,4*R*,5a*S*,6a*R*,10a*R*,10b*S*,10c*R*)-(3a,5a,6a,9,10,10a,10b,10c-Octahydro-2,2,6a-trimethyl-1,3,5,6-tetraoxa-9-oxo-4*H*-cyclopenta[*c*]fluoren-4-yl)methyl Ester (28).



27 **28**

A solution of Bu_3SnH (0.13 mL, 0.49 mmol) and AIBN (3.4 mg, 0.02 mmol) in PhH (5 mL) was added over 2 h by syringe pump to a stirred and heated (85 °C) solution of **27** (196 mg, 0.410 mmol) in PhH (5 mL). Heating was continued for 4 h after the addition. Evaporation of the solvent and flash chromatography of the residue over KF-flash chromatography silica gel (10%w/w KF), using 50% EtOAc-hexane, gave the cyclized product **28** (113 mg, 78%) as a white solid, which was a single isomer: mp 165-167 °C, $[\alpha]_D$ = 46.3 (*c* 0.51, $CHCl_3$); FTIR (microscope, cast) 2986, 2940, 1740, 1682, 1371, 1246 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.29 (s, 3 H), 1.45 (s, 3 H), 1.55 (s, 3 H), 2.05 (s, 3 H), 2.26 (ddd, *J* = 12.0, 8.0, 4.0 Hz, 1 H), 2.55 (dd, *J* = 17.5, 6.5 Hz, 1 H), 2.82 (ddt, *J* = 12.0, 6.0, 1.5 Hz, 1 H), 3.03 (ddd, *J* = 17.5, 1.5, 1.5 Hz, 1 H), 3.75 (ddd, *J* = 7.0, 4.0, 2.5 Hz, 1 H), 4.08 (dd, *J* = 7.0, 2.5 Hz, 1 H), 4.23 (dd, *J* = 12.0, 8.0 Hz, 1 H), 4.35 (dd, *J* = 12.0, 4.0 Hz, 1 H), 4.56 (dd, *J* = 7.5, 7.0 Hz, 1 H), 4.91 (d, *J* = 4.5 Hz, 1 H), 5.86 (dd, *J* = 10.5, 1.0 Hz, 1 H), 6.55 (dd, *J* = 10.0, 2.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.9 (q), 24.7 (q), 25.1 (q), 25.9 (q), 37.2 (t), 43.9 (d), 44.1 (d), 63.7 (t), 70.6 (d), 71.1 (d), 71.9 (d), 80.2 (s), 101.1 (d), 109.5 (s), 126.8 (d), 151.4 (d), 170.9 (s), 197.5 (s); exact mass (electrospray) *m*/*z* calcd for $C_{18}H_{24}NaO_7$ (M + Na) 375.1414, found 375.1413.

Acetic Acid (2*R*,3*R*,4*R*,4a*S*,4b*R*,8a*R*,9a*S*)-(3,4,4a,4b,5,6,8a,9a-Octahydro-3,4-dihydroxy-8a-methyl-6-oxo-2*H*-1,9-dioxafluoren-2-yl)methyl Ester (29).



28 **29**

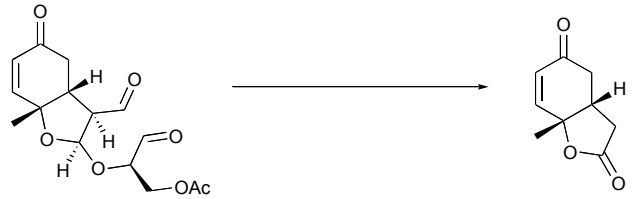
CF_3CO_2H (0.03 mL, 0.36 mmol) was added to a stirred and cooled (0 °C) solution of **28** (53.3 mg, 0.151 mmol) in 4:1 THF-water (2.5 mL). The ice bath was removed and stirring was continued for 12 h. Evaporation of the solvent and flash chromatography of the residue over silica gel (1 x 18 cm), using 50% EtOAc-hexane, gave **29** (38.6 mg, 81%) as a white solid: mp 145-147 °C, FTIR (microscope, cast) 3461, 2971, 2897, 1737, 1674, 1373, 1240 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.58 (s, 3 H), 2.05 (s, 3 H), 2.42 (ddd, *J* = 12.4, 6.0, 3.4 Hz, 1 H), 2.62 (dd, *J* = 17.1, 5.9 Hz, 1 H), 2.91 (s, 2 H), 3.17 (d, *J* = 17.4 Hz, 1 H), 3.35 (dd, *J* = 12.7, 6.0 Hz, 1 H), 3.54 (t, *J* = 6.5 Hz, 1 H), 3.79 (d, *J* = 3.7 Hz, 1 H), 4.08 (dd, *J* = 6.2, 4.0 Hz, 1 H), 4.22 (dd, *J* = 11.4, 6.5 Hz, 1 H), 4.46 (dd, *J* = 11.6, 6.2 Hz, 1 H), 5.01 (d, *J* = 3.4 Hz, 1 H), 5.86 (d, *J* = 10.3 Hz, 1 H), 6.57 (dd, *J* = 10.3, 1.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.9 (q), 25.6 (q), 37.6 (t), 43.3 (d), 46.9 (d), 63.3 (t), 67.4 (d), 68.7 (d), 71.2 (d), 82.4 (s), 101.0 (d), 126.0 (d), 151.8 (d), 171.6 (s), 198.6 (s); exact mass (electrospray) *m*/*z* calcd for $C_{15}H_{20}NaO_7$ (M + Na) 335.1101, found 375.1103.

Acetic Acid (2*R*)-2-[(2*S*,3*S*,3a*R*,7a*S*)-(3-Formyl-2,3,3a,4,5,7a-hexahydro-7a-methyl-5-oxobenzofuran-2-yl)oxy]-3-oxopropyl Ester (30).

29 **30**

Na_2CO_3 (28.9 mg, 0.273 mmol) and then $Pb(OAc)_4$ (60.5 mg, 0.137 mmol) were added to a stirred and cooled (-78 °C) solution of **29** (28.4 mg, 0.091 mmol) in CH_2Cl_2 (3 mL) and stirring was continued at -78 °C for 2 h. Evaporation of the solvent and flash chromatography of the residue over silica gel (1 x 16 cm), using 50% EtOAc-hexane, gave **30** (24 mg, 85%) as an oil: $[\alpha]_D$ = 26.1 (*c* 1.19, $CHCl_3$); FTIR (microscope, cast) 2971, 2931, 1739, 1681, 1374, 1236 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.60 (s, 3 H), 2.07 (s, 3 H), 2.65-2.77 (m, 2 H), 3.05 (ddd, *J* = 12.2, 5.1, 1.1 Hz, 1 H), 3.14-3.21 (m, 1 H), 4.34 (dd, *J* = 11.7, 4.8 Hz, 1 H), 4.42 (t, *J* = 4.8 Hz, 1 H), 4.50 (dd, *J* = 11.7, 3.9 Hz, 1 H), 5.50 (d, *J* = 5.0 Hz, 1 H), 5.89 (dd, *J* = 10.3, 0.6 Hz, 1 H), 6.51 (dd, *J* = 10.3, 1.8 Hz, 1 H), 9.64 (s, 1 H), 9.81 (d, *J* = 1.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.6 (q), 25.4 (q), 35.9 (t), 41.2 (d), 59.5 (d), 62.2 (t), 78.9 (d), 81.5 (s), 100.4 (d), 126.8 (d), 150.1 (d), 170.4 (s), 195.9 (s), 196.2 (d), 198.1 (d); exact mass (electrospray) *m*/*z* calcd for $C_{15}H_{18}NaO_7$ (M + Na) 333.0945, found 333.0942. The indicated stereochemistry α to the formyl groups was not proven.

(3a*R*,7a*S*)-3a,7a-Dihydro-7a-methyl-3*H*,4*H*-benzofuran-2,5-dione (31).

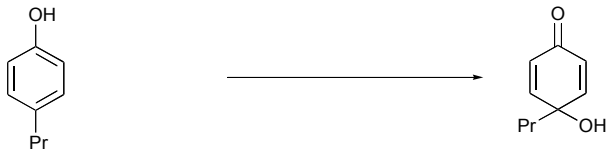


30 **31**

H_2SO_4 (0.1 M, 0.5 mL) was added to a stirred solution of **30** (55 mg, 0.18 mmol) in THF (3 mL) and stirring was continued for 4 h. The mixture was evaporated and the residue was used directly for the next step.

Jones reagent (ca 7.0 M, 0.076 mL, 0.532 mmol) was added to a stirred and cooled (-78 °C) solution of the above residue in acetone (5 mL) and stirring was continued for 30 min at -78 °C. The cold bath was removed and stirring was continued for 12 h. The mixture was quenched with MeOH (1 mL), diluted with EtOAc (5 mL), washed with aqueous NaOH (0.1N, 5 mL) and brine, dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (1 x 15 cm), using 30% EtOAc-hexane, gave **31** (19.7 mg, 67%) as a white solid: mp 114-115 °C, $[\alpha]_D$ = 29.1 (*c* 1.20, $CHCl_3$); FTIR (microscope, cast) 2979, 2932, 1776, 1683, 1379, 1254 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.69 (s, 3 H), 2.43 (dd, *J* = 17.5, 11.7 Hz, 1 H), 2.61 (dd, *J* = 17.3, 3.2 Hz, 1 H), 2.67-2.76 (m, 2 H), 2.89-2.98 (m, 1 H), 6.10 (dd, *J* = 10.3, 0.8 Hz, 1 H), 6.68 (dd, *J* = 10.3, 1.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.2 (q), 34.7 (t), 36.8 (t), 40.9 (d), 81.5 (s), 129.2 (d), 146.5 (d), 173.6 (s), 194.9 (s); exact mass (electrospray) *m*/*z* calcd for $C_9H_{10}NaO_3$ (M + Na) 189.0522, found 189.0522.

4-Hydroxy-4-propylcyclohexa-2,5-dienone (32).[4]

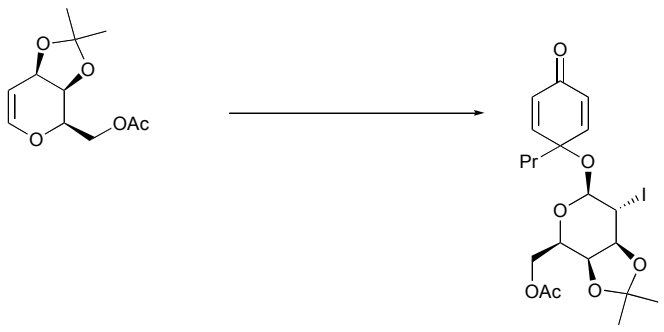


32

A mixture of Oxone (45.2 g, 73.4 mmol) and $NaHCO_3$ (18.5 g, 220 mmol) was added over ca 3 min to a vigorously stirred solution of *p*-propylphenol (2.00 g, 14.7 mmol) in MeCN (10 mL) and water (45 mL). The flask was immediately closed with a septum attached via a needle to an empty balloon to avoid loss of generated singlet oxygen. Vigorous stirring was

continued until all the phenol had reacted (TLC control). The mixture was diluted with water (20 mL), solid $Na_2S_2O_3$ (36.4 g, 147 mmol) was added and stirring was continued for 2 h. The mixture was then partitioned between EtOAc and water and the aqueous phase was extracted with EtOAc. The combined organic extracts were washed with brine, dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (2 x 25 cm), using 10% EtOAc-hexane, gave **32** (1.45 g, 65%) as an oil: FTIR (microscope, cast) 3390, 2962, 2935, 1700, 1670, 1396 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.92 (t, *J* = 7.3 Hz, 3 H), 1.27-1.33 (m, 2 H), 1.70-1.76 (m, 2 H), 2.33 (s, 1 H), 6.18 (dd, *J* = 10.2, 1.0 Hz, 2 H), 6.81 (dd, *J* = 10.2, 1.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.2 (q), 17.0 (t), 42.0 (t), 69.9 (s), 128.2 (d), 151.4 (d), 185.7 (s)); exact mass (electrospray) *m/z* calcd for $C_9H_{12}NaO_2$ (M + Na) 175.0729, found 175.0730.

4-Oxo-1-propylcyclohexa-2,5-dienyl 6-*O*-Acetyl-2-deoxy-2-iodo-3,4-*O*-(1-methyl-ethylidene)-β-D-galactopyranoside (32a).

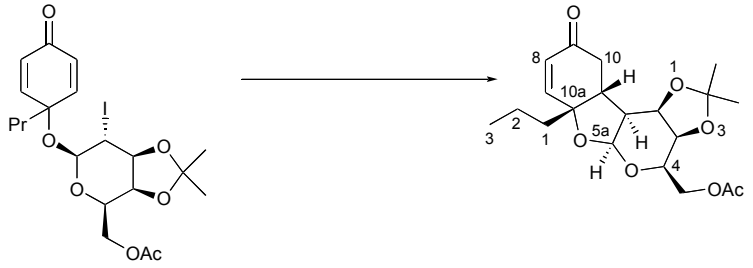


22 **32a**

NIS (309 mg, 1.37 mmol) was added to a stirred solution of **22** (157 mg, 0.69 mmol) in MeCN (5 mL) and the mixture was stirred at room temperature for 15 min. The cross conjugated enone **32** (115 mg, 0.752 mmol) was added and stirring was continued for 12 h. The mixture

was diluted with Et_2O, washed with saturated aqueous $Na_2S_2O_3$ and brine, dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (1.5 x 20 cm), using 30% EtOAc-hexane, gave **32a** (222 mg, 64%) as a white foam, which was an 18.4:1 mixture of isomers (^{1}H NMR): FTIR (microscope, cast) 2986, 2972, 1742, 1671, 1382, 1243 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.90 (t, *J* = 7.3 Hz, 3 H), 1.26-1.42 (m, 2 H), 1.32 (s, 3 H), 1.41 (s, 3 H), 1.68-1.80 (m, 2 H), 2.08 (s, 3 H), 3.76 (t, *J* = 8.9 Hz, 1 H), 3.83 (ddd, *J* = 8.0, 3.8, 2.1 Hz, 1 H), 3.87 (dd, *J* = 2.1, 5.1 Hz, 1 H), 4.18-4.31 (m, 3 H), 4.46 (dd, *J* = 8.9, 5.1 Hz, 1 H), 6.13 (dd, *J* = 10.2, 2.0 Hz, 1 H), 6.36 (dd, *J* = 9.2, 2.1 Hz, 1 H), 6.98 (d, *J* = 10.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.2 (d), 16.8 (t), 20.7 (q), 26.0 (q), 28.2 (q), 32.7 (q), 41.4 (t), 63.3 (t), 71.6 (d), 73.4 (d), 74.1 (s), 82.2 (d), 98.4 (d), 110.7 (s), 127.8 (d), 131.3 (d), 148.7 (d), 151.4 (d), 170.5 (s), 185.4 (s); exact mass (electrospray) *m*/*z* calcd for $C_{20}H_{27}INaO_7$ (M + Na) 529.0694, found 529.0694.

Acetic Acid (3a*S*,4*R*,5a*S*,6a*S*,10a*R*,10b*S*,10c*R*)-(3a,5a,6a,9,10,10a,10b,10c-Octahydro-2,2-dimethyl-1,3,5,6-tetra-oxa-9-oxo-6a-propyl-4*H*-cyclopenta[*c*]fluoren-4-yl)methyl Ester (32b).



32a **32b**

A solution of Bu_3SnH (0.06 mL, 0.23 mmol) and AIBN (1.6 mg, 0.01 mmol) in PhH (5 mL) was added over 2 h by syringe pump to a stirred and heated (85 °C) solution of **32a** (96 mg, 0.19 mmol) in PhH (5 mL). Heating was continued for 12 h after the addition. Evaporation of the solvent and flash chromatography of the residue over KF-flash chromatography silica gel (10%w/w KF), using 50% EtOAc-hexane, gave the cyclized product **32b** (57.4 mg, 80%) as an oil, which was a single isomer: $[\alpha]_D$ = 33.4 (*c* 0.51, $CHCl_3$); FTIR (microscope, cast) 2961, 2937, 1741, 1683, 1382, 1248 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.96 (t, *J* = 7.2 Hz, 3 H), 1.30 (s, 3 H), 1.46 (s, 3 H), 1.47-1.49 (m, 2 H), 1.71-1.79 (m, 1 H), 1.81-1.89 (m, 1 H), 2.03 (s, 3 H), 2.24 (ddd, *J* = 11.6, 7.8, 4.4 Hz, 1 H), 2.54 (dd, *J* = 17.6, 6.2 Hz, 1 H), 2.85-2.92 (m, 1 H), 3.02 (dd, *J* = 17.6, 1.2 Hz, 1 H), 3.74 (ddd, *J* = 6.9, 4.3, 2.6 Hz, 1 H), 4.08 (dd, *J* = 6.8, 2.6 Hz, 1 H), 4.25 (dd, *J* = 11.8, 7.5 Hz, 1 H), 4.35 (dd, *J* = 11.8, 4.3 Hz, 1 H), 4.56 (t, *J* = 7.0 Hz, 1 H), 4.91 (d, *J* = 4.5 Hz, 1 H), 5.92 (dd, *J* = 10.3, 1.0 Hz, 1 H), 6.58 (dd, *J* = 10.3, 1.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.5 (q), 17.2 (t), 20.9 (q), 24.8 (q), 26.0 (q), 37.6 (t), 40.9 (t), 42.0 (d), 44.1 (d), 63.7 (t), 70.7 (d), 71.0 (d), 72.0 (d), 82.4 (s), 100.9 (d), 109.5 (s), 127.5 (d), 151.0 (d), 170.9 (s), 197.8 (s); exact mass (electrospray) *m*/*z* calcd for $C_{20}H_{28}NaO_7$ (M + Na) 403.1727, found 403.1722.

TROESY measurements showed a correlation between C5a-**H** and C4-**H**, confirming the indicated syn arrangement. The signal for C5a-**H** is a doublet with *J* = 4.5 Hz, a value identical to that observed for **28**. The TROESY measurements did not show any correlation between C5a-**H** and C1-$\mathbf{H_2}$ of the propyl group, supporting the indicated anti relationship.

Acetic Acid (2*R*,3*R*,4*R*,4a*S*,4b*R*,8a*R*,9a*S*)-(3,4,4a,4b,5,6,8a,9a-Octahydro-3,4-dihydroxy-1,9-dioxa-6-oxo-8a-propyl-2*H*-fluoren-2-yl)methyl ester (pre-32c).

32b **pre-32c**

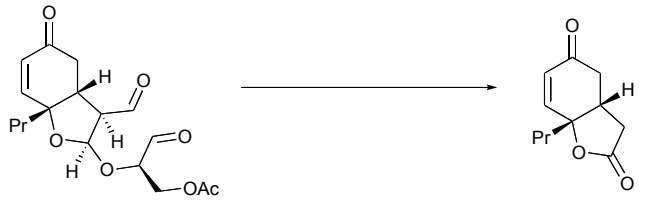
CF_3CO_2H (0.076 mL, 0.999 mmol) was added to a stirred and cooled (0 °C) solution of **32b** (45 mg, 0.12 mmol) in 4:1 THF-water (3 mL). The ice bath was removed and stirring was continued for 12 h. Evaporation of the solvent and flash chromatography of the residue over silica gel (1 x 10 cm), using 50% EtOAc-hexane, gave **pre-32c** (34.6 mg, 86%) as an oil: $[\alpha]_D$ = 9.5 (*c* 1.15, $CHCl_3$); FTIR (microscope, cast) 3461, 2962, 2903, 1738, 1675, 1373, 1240 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.97 (t, *J* = 7.3 Hz, 3 H), 1.48-1.54 (m, 2 H), 1.77-1.83 (m, 2 H), 2.07 (s, 3 H), 2.39-2.46 (m, 3 H), 2.60 (dd, *J* = 17.4, 6.3 Hz, 1 H), 3.15 (d, *J* = 17.4 Hz, 1 H), 3.36 (dd, *J* = 12.3, 6.2 Hz, 1 H), 3.52 (t, *J* = 6.4 Hz, 1 H), 3.76 (d, *J* = 3.6 Hz, 1 H), 4.06 (dd, *J* = 6.0, 3.9 Hz, 1 H), 4.18 (dd, *J* = 11.4, 6.2 Hz, 1 H), 4.48 (dd, *J* = 11.5, 6.8 Hz, 1 H), 4.98 (d, *J* = 3.6 Hz, 1 H), 5.85 (d, *J* = 10.3 Hz, 1 H), 6.58 (dd, *J* = 10.3, 1.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.5 (q), 17.2 (t), 20.9 (q), 38.0 (t), 41.3 (t), 41.5 (d), 47.1 (d), 63.0 (t), 67.4 (d), 68.8 (d), 71.0 (d), 84.7 (s), 100.7 (d), 126.7 (d), 151.1 (d), 171.6 (s), 198.8 (s); exact mass (electrospray) *m*/*z* calcd for $C_{17}H_{24}NaO_7$ (M + Na) 363.1414, found 363.1414.

Acetic Acid (2*R*)-2-[(2*S*,3*S*,3a*R*,7a*S*)-2-[(3-Formyl-2,3,3a,4,5,7a-hexahydro-5-oxo-7a-propylbenzo-furan-2-yl)oxy]-3-oxopropyl Ester (32c).

pre-32c **32c**

Na_2CO_3 (14.3 mg, 0.135 mmol) and then $Pb(OAc)_4$ (29.9 mg, 0.067 mmol) were added to a stirred and cooled (-78 °C) solution of **pre-32c** (15.3 mg, 0.045 mmol) in CH_2Cl_2 (2 mL) and stirring was continued at -78 °C for 5 h. Evaporation of the solvent and flash chromatography of the residue over silica gel (1 x 10 cm), using 50% EtOAc-hexane, gave **32c** (12.2 mg, 80%) as an oil: $[\alpha]_D$ = 28.9 (*c* 0.92, $CHCl_3$); FTIR (microscope, cast) 2962, 2935, 1741, 1682, 1382, 1240 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 0.99 (t, *J* = 7.1 Hz, 3 H), 1.26-1.32 (m, 1 H), 1.44-1.56 (m, 2 H), 1.72-1.82 (m, 1 H), 1.86-1.94 (m, 1 H), 2.04 (s, 3 H), 2.67-2.74 (m, 2 H), 3.18-3.23 (m, 1 H), 3.41 (dd, *J* = 12.2, 5.1 Hz, 1 H), 4.36 (dd, *J* = 11.3, 4.1 Hz, 1 H), 4.42-4.48 (m, 1 H), 5.51 (d, *J* = 4.8 Hz, 1 H), 5.94 (d, *J* = 10.3 Hz, 1 H), 6.54 (d, *J* = 10.3 Hz, 1 H), 9.64 (s, 1 H), 9.81 (s, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.5 (q), 17.4 (t), 20.6 (q), 36.4 (t), 39.5 (d), 41.5 (t), 59.8 (d), 62.2 (t), 78.9 (d), 83.8 (s), 100.2 (d), 127.6 (d), 149.7 (d), 170.4 (s), 196.2 (s), 196.3 (d), 198.1 (d); exact mass (electrospray) *m*/*z* calcd for $C_{17}H_{22}NaO_7$ (M + Na) 361.0945, found 361.0942. The indicated stereochemistry α to the formyl groups was not proven.

(3a*R*,7a*S*)-3a,7a-Dihydro7a-propyl-3*H*,4*H*-benzofuran-2,5-dione (32d).

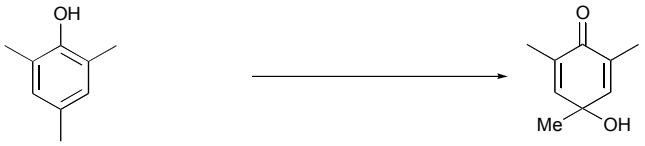


32c **32d**

H_2SO_4 (0.1 M, 0.2 mL) was added to a stirred solution of **32c** (10.4 mg, 0.031 mmol) in THF (1.5 mL) and stirring was continued for 6 h. The mixture was evaporated and the residue was used directly for the next step.

Jones reagent (ca 7.0 M, 0.013 mL, 0.093 mmol) was added to a stirred and cooled (-78 °C) solution of the above residue in acetone (2 mL) and stirring was continued for 30 min at -78 °C. The cold bath was removed and stirring was continued for 12 h. The mixture was quenched with MeOH (1 mL), diluted with EtOAc (5 mL), washed with aqueous NaOH (0.1 N, 5 mL), and brine, dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (1 x 12 cm), using 30% EtOAc-hexane, gave **32d** (3.9 mg, 64%) as an oil: $[\alpha]_D$ = 30.2 (*c* 2.59, $CHCl_3$); FTIR (microscope, cast) 2963, 2875, 1780, 1685, 1228 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.03 (t, *J* = 7.3 Hz, 3 H), 1.51-1.57 (m, 2 H), 1.82-1.87 (m, 1 H), 1.92-1.97 (m, 1 H), 2.42 (dd, *J* = 17.5, 11.9 Hz, 1 H), 2.60 (dd, *J* = 17.5, 2.9 Hz, 1 H), 2.65-2.76 (m, 2 H), 2.93-3.20 (m, 1 H), 6.13 (dd, *J* = 10.4, 1.0 Hz, 1 H), 6.68 (dd, *J* = 10.4, 1.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.3 (q), 17.1 (t), 34.8 (t), 37.1 (t), 38.9 (d), 40.0 (t), 83.8 (s), 129.7 (d), 145.9 (d), 173.8 (s), 195.1 (s); exact mass) *m/z* calcd for $C_{11}H_{14}O_3$ 194.0943, found 194.0942.

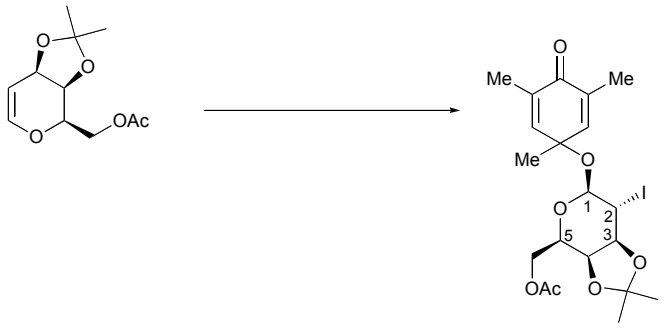
4-Hydroxy-2,4,6-trimethylcyclohexa-2,5-dienone (33).[4]



33

A mixture of Oxone (45.2 g, 73.4 mmol) and $NaHCO_3$ (18.5 g, 220 mmol) was added over ca 3 min to a vigorously stirred solution of 2,4,6-trimethylphenol (2.00 g, 14.7 mmol) in MeCN (10 mL) and water (43 mL). The flask was immediately closed with a septum attached via a needle to an empty balloon to avoid loss of generated singlet oxygen. Vigorous stirring was continued until all the phenol had reacted (TLC control). The mixture was diluted with water (20 mL), solid $Na_2S_2O_3$ (36.4 g, 147 mmol) was added and stirring was continued for 1 h. The mixture was then partitioned between EtOAc and water and the aqueous phase was extracted with EtOAc. The combined organic extracts were washed with brine, dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (2 x 22 cm), using 10% EtOAc-hexane, gave **33** (1.92 g, 86%) as a pale yellow solid: mp 41-43 °C, FTIR (microscope, cast) 3410, 2978, 2925, 1674, 1640, 1373, 1210 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.34 (s, 3 H), 1.75 (s, 6 H), 3.18 (s, 1 H), 6.56 (s, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.7 (q), 27.0 (q), 66.9 (s), 132.9 (s), 148.0 (d), 187.0 (s).

1,3,5-Trimethyl-4-oxocyclohexa-2,5-dienyl 6-*O*-Acetyl-2-deoxy-2-iodo-3,4-*O*-(1-methylethylidene)-β-D-galactopyranoside (33a).

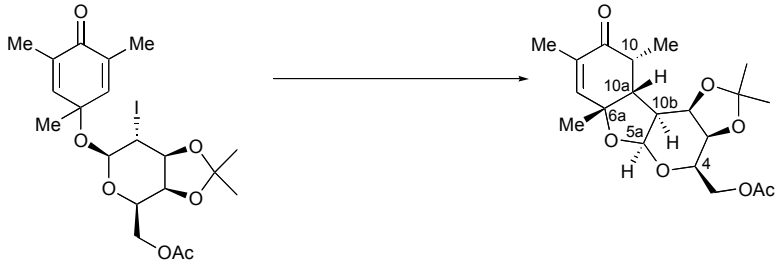


22 **33a**

NIS (371 mg, 1.65 mmol) was added to a stirred solution of **22** (313 mg, 1.37 mmol) in MeCN (10 mL) and the mixture was stirred at room temperature for 15 min. The cross conjugated enone **33** (261 mg, 1.72 mmol) was added and stirring was continued for 12 h. The mixture was diluted with Et_2O, washed with saturated aqueous $Na_2S_2O_3$ and brine, dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (1.5 x 19 cm), using 30% EtOAc-hexane, gave **33a** (463 mg, 67%) as a yellow oil, which was a single isomer: $[\alpha]_D$ = -4.4 (*c* 9.4, $CHCl_3$); FTIR (microscope, cast) 2985, 2930, 1743, 1674, 1643, 1372, 1243 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.31 (s, 3 H), 1.38 (s, 3 H), 1.39 (s, 3 H), 1.89 (d, *J* = 1.3 Hz, 3 H), 1.92 (d, *J* = 1.3 Hz, 3 H), 2.05 (s, 3 H), 3.76 (t, *J* = 9.2 Hz, 1 H), 3.82 (ddd, *J* = 7.6, 3.8, 2.2 Hz, 1 H), 3.86 (dd, *J* = 5.0, 2.1 Hz, 1 H), 4.12 (d, *J* = 9.5 Hz, 1 H), 4.20 (dd, *J* = 12.0, 7.6 Hz, 1 H), 4.30 (dd, *J* = 12.0, 3.9 Hz, 1 H), 4.46 (dd, *J* = 8.8, 5.0 Hz, 1 H), 6.76-6.77 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.8 (q), 16.0 (q), 20.9 (q), 26.0 (q), 26.2 (q), 28.2 (q), 33.1 (d), 63.7 (t), 71.5 (d), 73.5 (d), 74.3 (s), 82.2 (d), 98.1 (d), 110.5 (s), 134.0 (s), 136.3 (s), 144.9 (d), 146.2 (d), 170.6 (s), 186.6 (s); exact mass (electrospray) *m*/*z* calcd for $C_{20}H_{27}INaO_7$ (M + Na) 529.1000, found 529.1001.

TROESY measurements showed correlations between C1-**H** and C5-**H**, and between C1-**H** and C3-**H**; the signal for C1-**H** was a doublet with J = 9.5 Hz; these data are consistent with the indicated stereochemistry.

Acetic Acid (3a*R*,4*R*,5a*S*,6a*S*,10*R*,10a*S*,10b*S*,10c*R*)-(3a,5a,6a,9,10,10a,10b,-10c-Octahydro-2,2,6a,8,10-pentamethyl-1,3,5,6-tetraoxa-9-oxo-4*H*-cyclopenta[*c*]fluoren-4-yl)methyl Ester (33b).



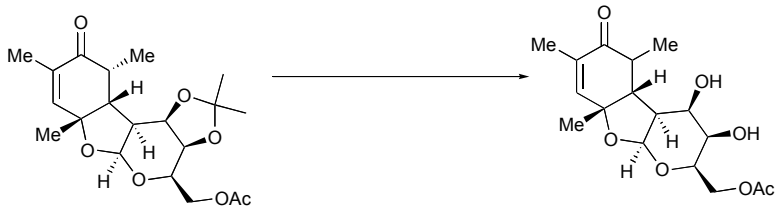
33a **33b**

A solution of Bu_3SnH (0.06 mL, 0.23 mmol) and AIBN (1.61 mg, 0.01 mmol) in PhH (5 mL) was added over 2 h by syringe pump to a stirred and heated (85 °C) solution of **33a** (98.9 mg, 0.19 mmol) in PhH (5 mL). Heating was continued for 10 h after the addition. Evaporation of the solvent and flash chromatography of the residue over KF-flash chromatography silica gel (10%w/w KF), using 70% EtOAc-hexane, gave the cyclized product **33b** (59.4 mg, 80%) as a white foam, which was a single isomer: $[\alpha]_D$ = -16.0 (*c* 2.88, $CHCl_3$); FTIR (microscope, cast) 2980, 2935, 1741, 1680, 1369, 1241 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.17 (d, J = 6.8 Hz, 3 H), 1.27 (s, 3 H), 1.44 (s, 3 H), 1.51 (s, 3 H), 1.71 (s, 3 H), 1.72-1.79 (m, 1 H), 2.00 (s, 3 H), 2.99 (ddd, J = 13.4, 6.8, 6.8 Hz, 1 H), 2.97-3.00 (m, 1 H), 3.44-3.47 (m, 1 H), 4.31-4.43 (m, 2 H), 4.51 (dd, J = 11.9, 4.2 Hz, 1 H), 4.69 (t, J = 6.2 Hz, 1 H), 5.18 (d, J = 6.6 Hz, 1 H), 6.26 (s, 1 H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.0 (q), 15.6 (q), 23.2 (q), 25.0 (q), 25.1 (q), 26.6 (q), 40.6 (d), 41.5 (d), 49.7 (d), 63.2 (t), 71.6 (d), 72.5 (d), 73.3 (d), 79.1 (s), 101.4 (d), 109.0 (s), 134.9 (s), 145.6 (d), 170.9 (s), 200.7 (s); exact mass (electrospray) *m*/*z* calcd for $C_{20}H_{28}NaO_7$ (M + Na) 403.1727, found 403.1726.

TROESY measurements showed the expected correlations between C5a-**H** and C4-**H**; C6a-Me and C10a-**H**; C6a-Me and C10-**H**. No correlation was observed between C6a-Me and C5a-**H**.

Acetic Acid (2*R*,3*R*,4*R*,4a*S*,4b*S*,8a*S*)-(3,4,4a,4b,5,6,8a,9a-Octahydro-3,4-dihydroxy-5,7,8a-trimethyl-6-oxo-2*H*-1,9-dioxafluoren-2-yl)methyl Ester (pre-33c).



33b **pre-33c**

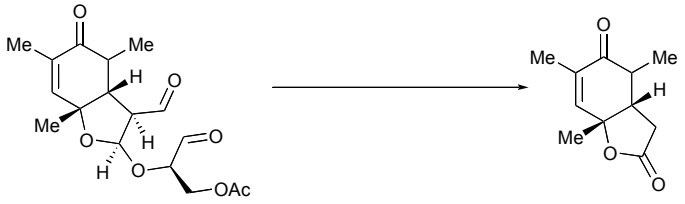
CF_3CO_2H (0.06 mL, 0.789 mmol) was added to a stirred and cooled (0 °C) solution of **33b** (150 mg, 0.395 mmol) in 4:1 THF-water (3 mL). The ice bath was removed and stirring was continued for 12 h. Evaporation of the solvent gave crude **pre-33c**, which was used directly for the next step. The material had: FTIR (microscope, cast) 3472, 2979, 2934, 1743, 1679, 1379, 1247 cm^{-1}.

Acetic Acid (2*R*)-2-[(2*S*,3*S*,3a*R*,7a*S*)-(3-Formyl-2,3,3a,4,5,7a-hexahydro-4,6,7a-trimethyl-5-oxobenzofuran-2-yl)oxy]-3-oxopropyl Ester (33c).

pre-33c **33c**

$Pb(OAc)_4$ (262 mg, 0.592 mmol) was added to a stirred and cooled (-78 °C) solution of crude **pre-33c** (all the material from the previous step, 0.395 mmol) in CH_2Cl_2 (5 mL) and stirring was continued at -78 °C for 5 h. Evaporation of the solvent gave crude **33c**, which was used directly for the next step. The indicated stereochemistry α to the formyl groups was not proven.

(3a*S*,7a*S*)-3a,7a-Dihydro-4,6,7a-trimethyl-3*H*,4*H*-benzofuran-2,5-dione (33d).

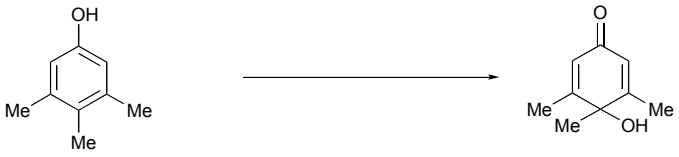


33c **33d**

H_2SO_4 (0.1 M, 1.0 mL) was added to a stirred solution of crude **33c** (all the material from the previous step, 0.395 mmol) in THF (3 mL) and stirring was continued for 6 h. The mixture was evaporated and the residue was used directly for the next step.

Jones reagent (ca 7.0 M, 0.17 mL, 1.2 mmol) was added to a stirred and cooled (-78 °C) solution of the above residue in acetone (3 mL) and stirring was continued for 30 min at -78 °C. The cold bath was removed and stirring was continued for 12 h. The mixture was quenched with MeOH (1 mL), diluted with EtOAc (5 mL), washed with aqueous NaOH (0.1 N, 5 mL) and brine, dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (1 x 12 cm), using 10% EtOAc-hexane, gave **33d** (40.6 mg, 53%) as an oil: $[\alpha]_D$ = -54.1 (*c* 0.51, $CHCl_3$); FTIR (microscope, cast) 2924, 2852, 1771, 1682, 1684, 1381, 1221 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.18 (d, *J* = 6.7 Hz, 3 H), 1.62 (s, 3 H), 1.83 (s, 3 H), 2.08-2.22 (m, 2 H), 2.61 (dd, *J* = 16.8, 8.3 Hz, 1 H), 2.75-2.86 (m, 1 H), 6.34 (s, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.4 (q), 15.8 (q), 24.3 (q), 32.1 (t), 40.9 (d), 48.2 (d), 82.9 (s), 136.1 (s), 140.8 (d), 179.9 (s), 192.7 (s); exact mass *m*/*z* calcd for $C_{11}H_{14}O_3$ 194.0943, found 194.0941.

4-Hydroxy-3,4,5-trimethylcyclohexa-2,5-dienone (34).[4]

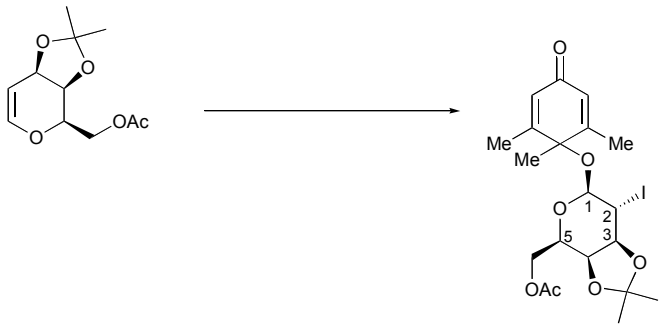


34

A mixture of Oxone (45.2 g, 73.4 mmol) and $NaHCO_3$ (18.5 g, 220 mmol) was added over ca 3 min to a vigorously stirred solution of 3,4,5-trimethylphenol (2.00 g, 14.7 mmol) in MeCN (20 mL) and water (32 mL). The flask was immediately closed with a septum attached via a needle to an empty balloon to avoid loss of generated singlet oxygen. Vigorous stirring was continued until all the phenol had reacted (TLC control). The mixture was diluted with

water (15 mL), solid $Na_2S_2O_3$ (36.5 g, 147 mmol) was added and stirring was continued for 2 h. The mixture was then partitioned between EtOAc and water and the aqueous phase was extracted with EtOAc. The combined organic extracts were washed with brine, dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (2 x 20 cm), using 50% EtOAc-hexane, gave **34** (1.81 g, 81%) as a white solid: mp 66-68 °C, FTIR (microscope, cast) 3265, 2989, 2923, 1666, 1610, 1381, 1167 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.30 (s, 3 H), 1.98 (s, 6 H), 4.33 (s, 1 H), 5.75 (s, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.2 (q), 26.1 (q), 71.4 (s), 125.1 (d), 165.0 (s), 186.1 (s); exact mass *m/z* calcd for $C_9H_{12}O_2$ 152.0837, found 152.0837.

3,4,5-Trimethyl-4-oxocyclohexa-2,5-dienyl 6-*O*-Acetyl-2-deoxy-2-iodo-3,4-*O*-(1-methylethylidene)-β-D-galactopyranoside (34a).



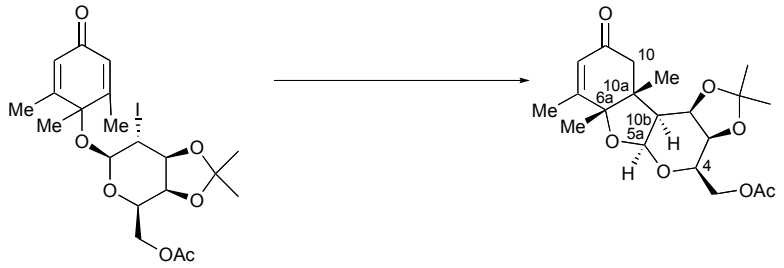
22 **34a**

NIBS (338 mg, 1.50 mmol) was added to a stirred solution of **22** (171 mg, 0.75 mmol) in MeCN (10 mL) and the mixture was stirred at room temperature for 15 min. The cross conjugated enone **34** (123 mg, 0.83 mmol) was added and stirring was continued for 12 h. The mixture was diluted with Et_2O, washed with saturated aqueous $Na_2S_2O_3$ and brine, dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (2.0 x 19 cm),

using 30% EtOAc-hexane, gave **34a** (240 mg, 63%) as an oil, which was a single isomer: $[\alpha]_D$ = 53.3 (*c* 0.48, $CHCl_3$); FTIR (microscope, cast) 2992, 2926, 1738, 1670, 1620, 1374, 1241 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.32 (s, 3 H), 1.48 (s, 3 H), 1.51 (s, 3 H), 2.07 (s, 6 H), 2.21 (s, 3 H), 3.72-3.75 (m, 1 H), 3.78 (t, *J* = 9.1 Hz, 1 H), 3.87 (dd, *J* = 5.1, 2.2 Hz, 1 H), 4.06 (dd, *J* = 12.1, 8.2 Hz, 1 H), 4.21 (d, *J* = 9.1 Hz, 1 H), 4.29 (dd, *J* = 12.1, 2.9 Hz, 1 H), 4.45 (dd, *J* = 9.0, 5.1 Hz, 1 H), 5.94 (d, *J* = 1.3 Hz, 1 H), 6.20 (d, *J* = 1.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) (1 quaternary carbon missing) δ 19.3 (q), 19.4 (q), 20.8 (q), 24.5 (q), 26.0 (q), 28.2 (q), 32.0 (d), 63.5 (t), 72.0 (d), 73.5 (d), 82.1 (d), 98.4 (d), 110.5 (s), 125.5 (d), 130.9 (d), 156.6 (s), 163.3 (s), 171.0 (s), 185.3 (s); exact mass (electrospray) *m*/*z* calcd for $C_{20}H_{27}INaO_7$ (M + Na) 529.0694, found 529.0694.

The signal for C1-**H** is a doublet, *J* = 9.1 Hz, consistent with the indicated stereochemistry.

Acetic Acid (3a*R*,4*R*,5a*S*,6a*R*,10a*R*,10b*S*,10c*R*)-(3a,5a,6a,9,10,10a,10b,10c-Octahydro-2,2,6a,7,10a-pentamethyl-1,3,5,6-tetraoxa-9-oxo-4*H*-cyclopenta[*c*]-fluoren-4-yl)methyl Ester (34b).



34a **34b**

A solution of Bu_3SnH (0.12 mL, 0.46 mmol) and AIBN (3.2 mg, 0.02 mmol) in PhH (5 mL) was added over 2 h by syringe pump to a stirred and heated (85 °C) solution of **34a** (196 mg, 0.39 mmol) in PhH (5 mL). Heating was continued for 12 h after the addition. Evaporation of the solvent and flash chromatography of the residue over KF-flash chromatography silica gel (10%w/w KF), using 50% EtOAc-hexane, gave the cyclized product **34b** (109 mg, 74%) as a pale yellow oil: $[\alpha]_D$ = 62.9 (*c* 1.99, $CHCl_3$); FTIR (microscope, cast) 2983, 2935, 1739, 1664, 1372, 1242 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.18 (s, 3 H), 1.26 (s, 3 H), 1.33 (s, 3 H), 1.38 (s, 3 H), 2.03 (s, 3 H), 2.08 (s, 3 H), 2.09-2.12 (m, 1 H), 2.57 (AB q, J = 18.6 Hz, $\Delta\nu_{AB}$ = 289.6 Hz, 2 H), 3.40-3.44 (m, 1 H), 4.08-4.15 (m, 2 H), 4.28 (dd, J = 12.0, 4.2 Hz, 1 H), 4.41 (dd, J = 4.9, 6.7 Hz, 1 H), 5.31 (d, J = 6.7 Hz, 1 H), 5.76 (s, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 19.6 (q), 21.0 (q), 22.9 (q), 24.6 (q), 26.3 (q), 30.5 (q), 43.4 (t), 47.4 (s), 49.9 (d), 63.3 (t), 70.8 (d), 72.0 (d), 72.5 (d), 85.6 (s), 102.3 (d), 109.6 (s), 127.4 (d), 162.4 (s), 171.0 (s), 195.7 (s); exact mass (electrospray) m/z calcd for $C_{20}H_{28}NaO_7$ (M + Na) 403.1727, found 403.1729.

TROESY measurements showed correlations between C5a-**H** and C4-**H**; and between the C6a-**Me** and the C10a-**Me**. No correlation was observed between C6a-Me and C5a-**H**.

Acetic Acid (2*R*,3*R*,4*R*,4a*S*,4b*R*,8a*R*,9a*S*)-(3,4,4a,4b,5,6,8a,9a-Octahydro-3,4-dihydroxy-4b,8,8a-trimethyl-6-oxo-2*H*-1,9-dioxafluoren-2-yl)methyl Ester (pre-34c).

34b **pre-34c**

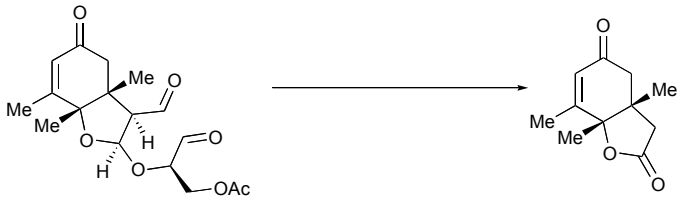
CF_3CO_2H (0.06 mL, 0.84 mmol) was added to a stirred and cooled (0 °C) solution of **34b** (106 mg, 0.279 mmol) in 4:1 THF-water (3 mL). The ice bath was removed and stirring was continued for 12 h. Evaporation of the solvent gave crude **pre-34c**, which was used directly for the next step.

Acetic Acid (2*R*)-2-[(2*S*,3*S*,3a*R*,7a*S*)-(3-Formyl-2,3,3a,4,5,7a-hexahydro-3a,7,7a-trimethyl-5-oxobenzofuran-2-yl)oxy]-3-oxopropyl Ester (34c).

pre-34c **34c**

$Pb(OAc)_4$ (185 mg, 0.418 mmol) was added to a stirred and cooled (-78 °C) solution of crude **pre-34c** (all material from previous step, 0.279 mmol) in CH_2Cl_2 (4 mL) and stirring was continued at -78 °C for 4 h. Evaporation of the solvent gave crude **34c**, which was used directly for the next step. The indicated stereochemistry α to the formyl groups was not proven.

(3a*R*,7a*S*)-3a,7a-Dihydro-3a,7,7a-trimethyl-3*H*,4*H*-benzofuran-2,5-dione (34d).



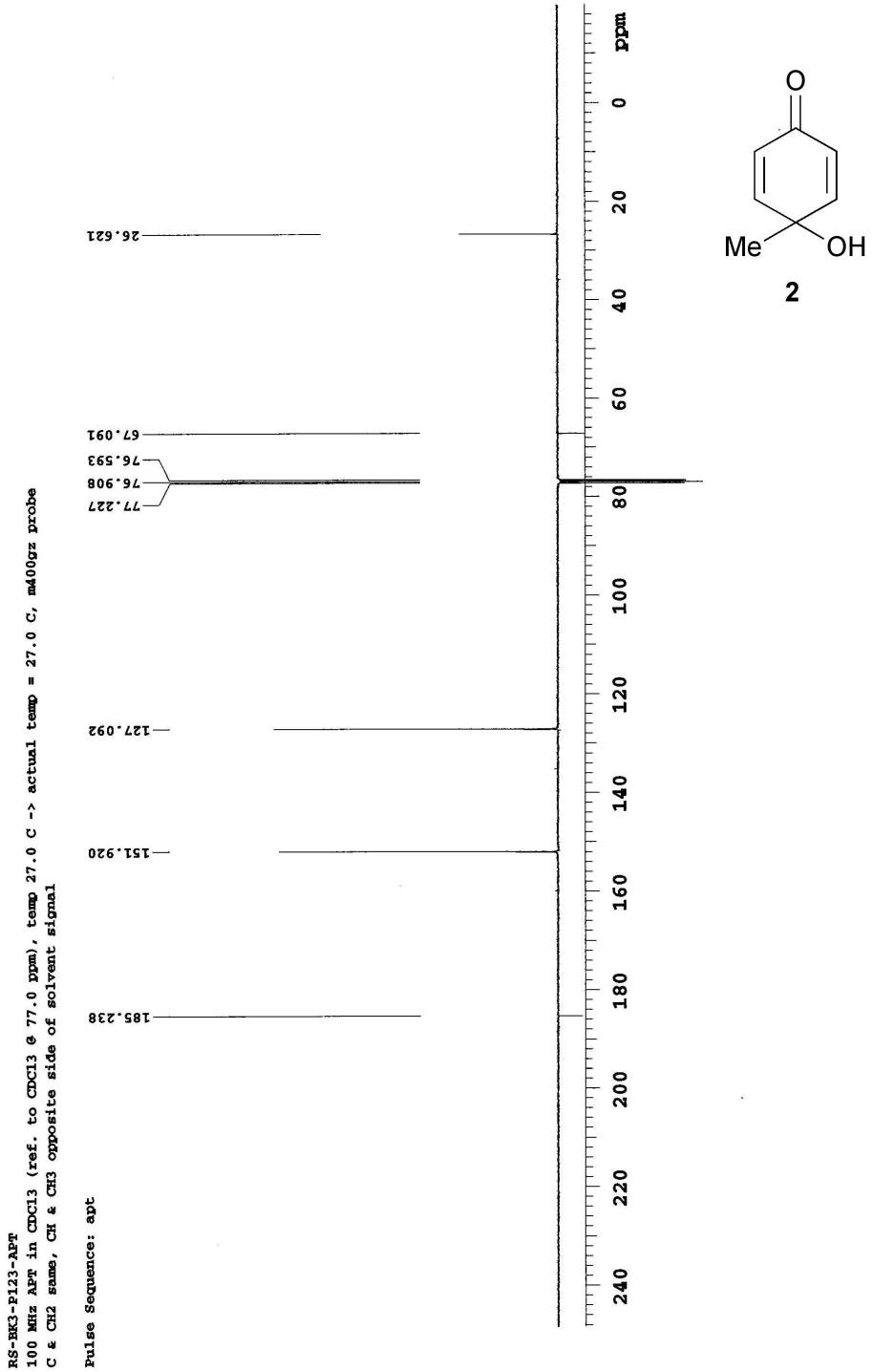
34c **34d**

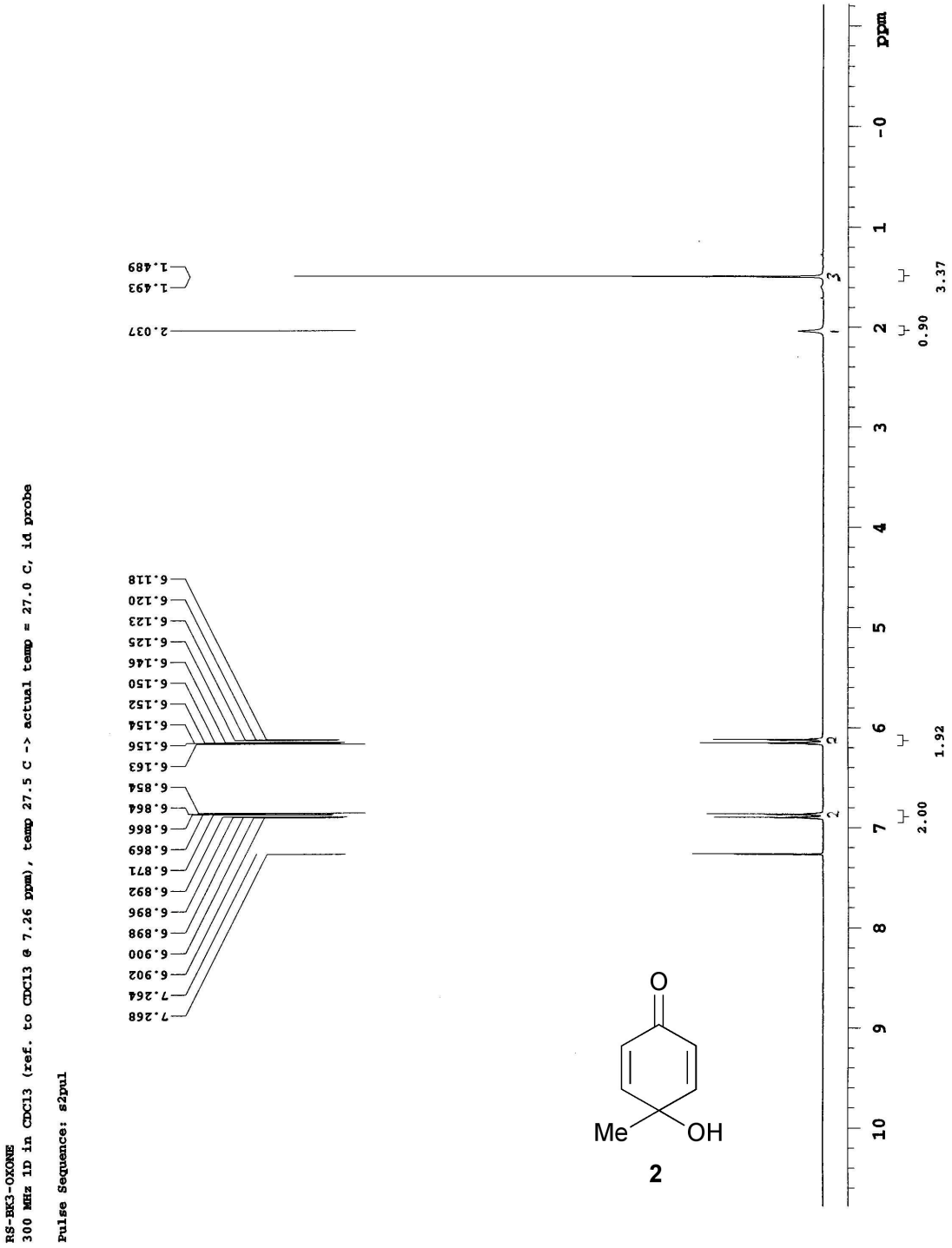
H_2SO_4 (0.1 M, 0.5 mL) was added to a stirred solution of crude **34c** (all material from previous step, 0.279 mmol) in THF (2 mL) and stirring was continued for 5 h. The mixture was evaporated and the residue was used directly for the next step.

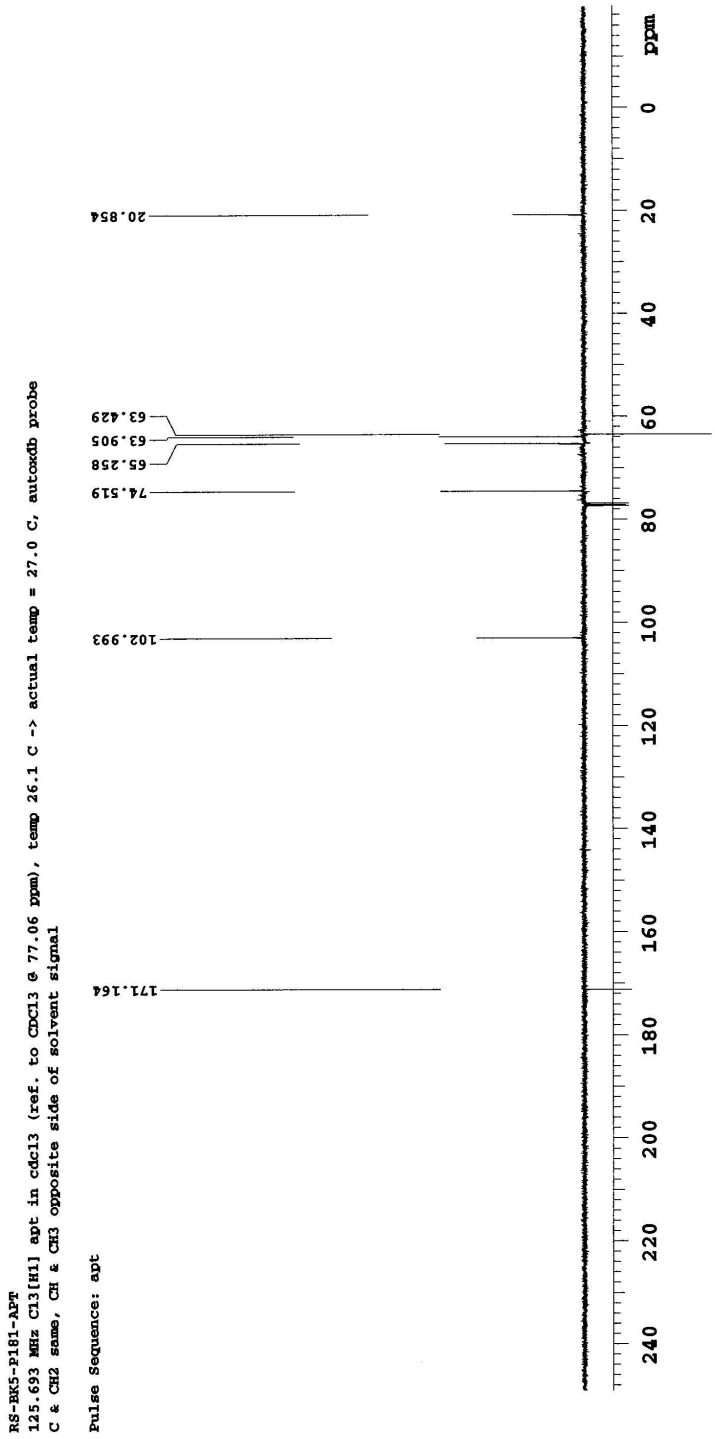
Jones reagent (ca 7.0 M, 0.12 mL, 0.84 mmol) was added to a stirred and cooled (-78 °C) solution of the above residue in acetone (2 mL) and stirring was continued for 30 min at -78 °C. The cold bath was removed and stirring was continued for 8 h. The mixture was quenched with MeOH (1 mL), diluted with EtOAc (5 mL), washed with aqueous NaOH (0.1 N, 4 mL) and brine, dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (1 x 15 cm), using 30% EtOAc-hexane, gave **34d** (33.5 mg, 62%) as an oil: $[\alpha]_D$ = 54.1 (*c* 0.33, $CHCl_3$); FTIR (microscope, cast) 2925, 2859, 1781, 1681, 1378, 1236 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.25 (s, 3 H), 1.56 (s, 3 H), 2.12 (s, 3 H), 2.47 (ABq, J = 17.0 Hz, $\Delta\nu_{AB}$ = 162.6 Hz, 2 H), 2.50 (ABq, J = 17.3 Hz, $\Delta\nu_{AB}$ = 50.2 Hz, 2 H), 5.98 (s, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.2 (q), 18.7 (q), 23.9 (q), 41.5 (t), 43.6 (s), 44.0 (t), 86.1 (s), 127.9 (d), 158.7 (s), 173.8 (s), 195.0 (s); exact mass *m*/*z* calcd for $C_{11}H_{14}O_3$ 194.0943, found 194.0939.

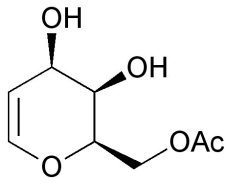
Reference

17 E. W. Holla, *Angew. Chem. Int.* 1989, *28*, 220-221.

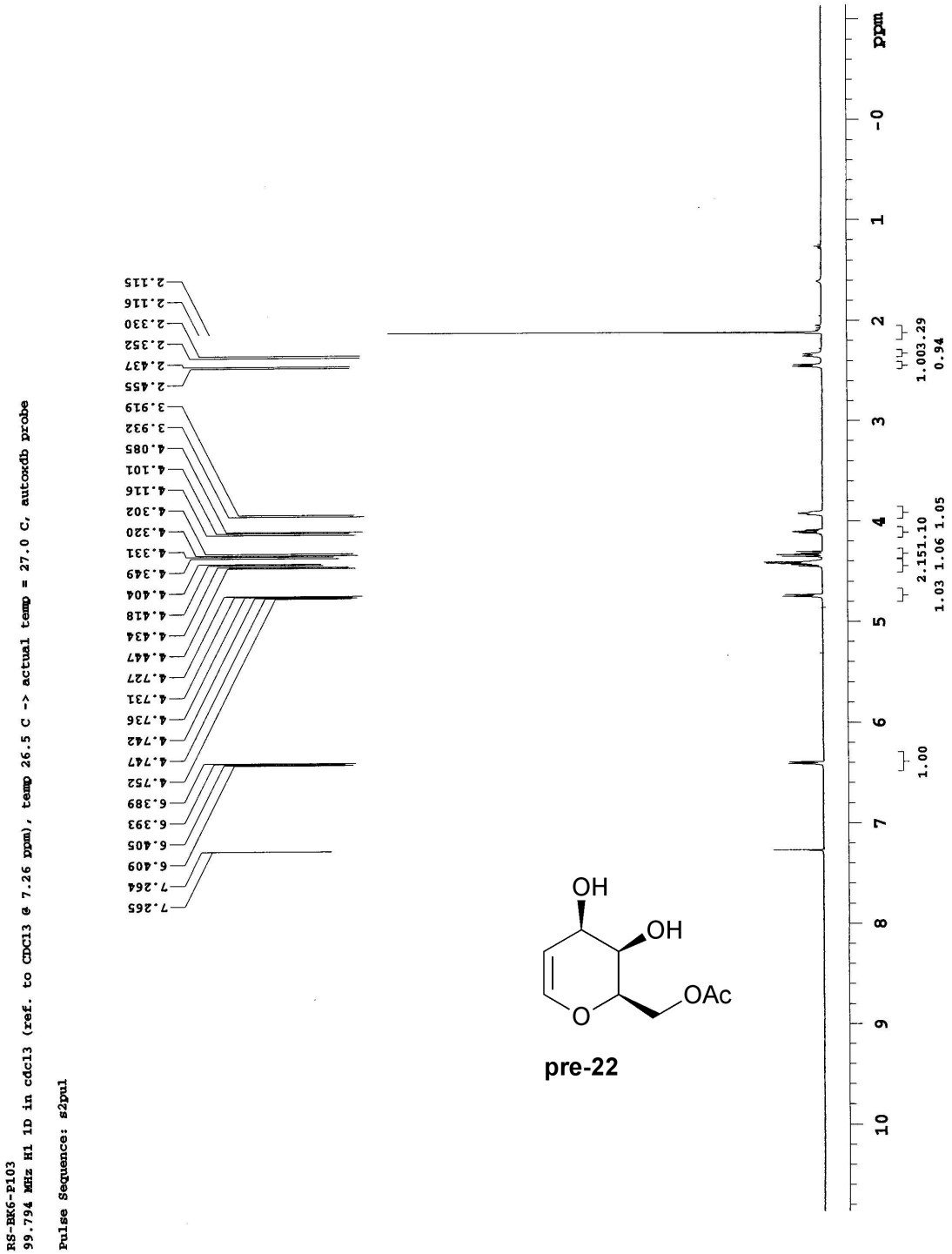

RS-BK3-P123-APT
100 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm), temp 27.0 C -> actual temp = 27.0 C, m400gz probe
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: apt
26.621
67.091
76.593
76.908
77.227
127.092
151.920
185.238
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
O
Me
OH
2

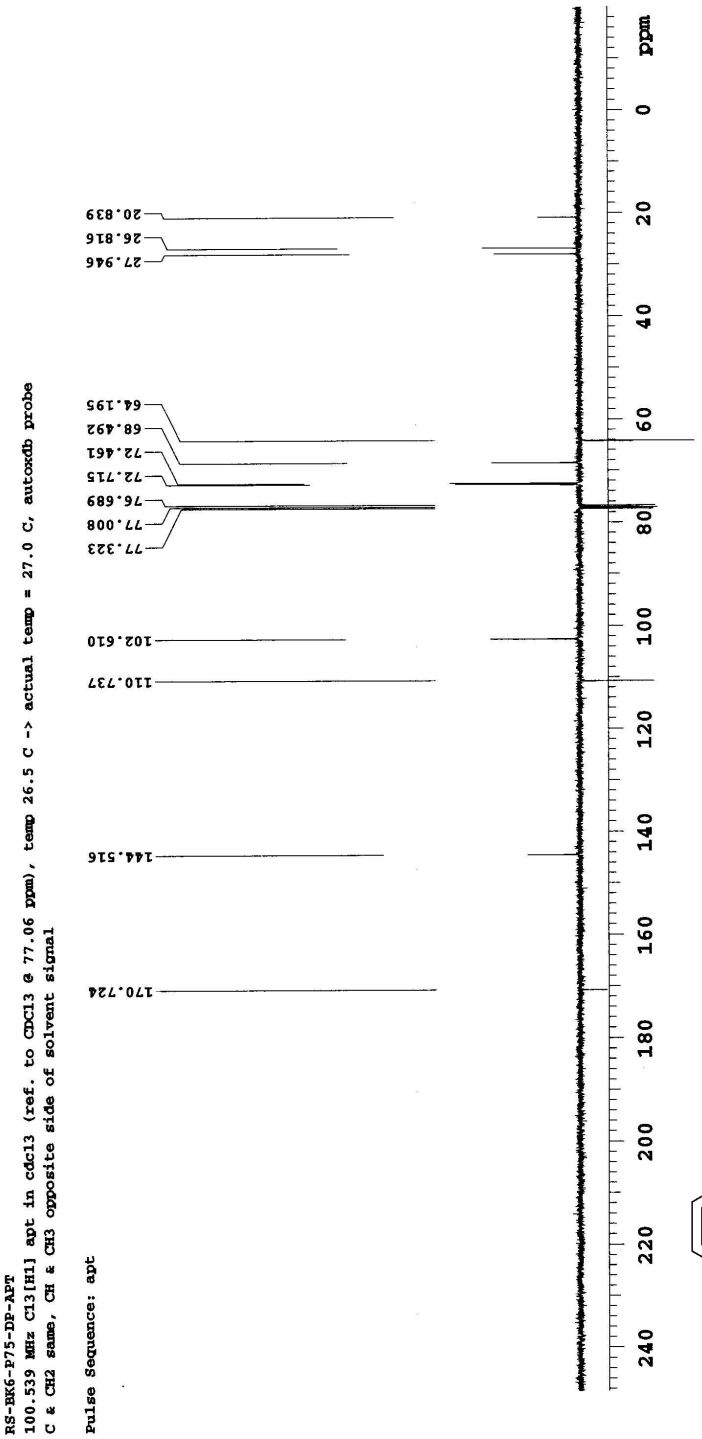

RS-EK3-OXONE
300 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.5 C -> actual temp = 27.0 C, id probe
Pulse Sequence: s2pul
1.489
1.493
2.037
6.118
6.120
6.123
6.125
6.146
6.150
6.152
6.154
6.156
6.163
6.854
6.864
6.866
6.869
6.871
6.892
6.896
6.898
6.900
6.902
7.264
7.268
ppm
3.37
0.90
1.92
2.00
O
Me
OH
2

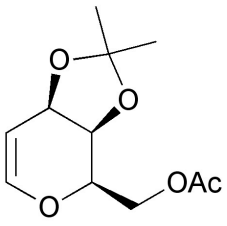

RS-BK5-P181-APT
125.693 MHz C13[H1] apt in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: apt
20.854
63.429
63.905
65.258
74.519
102.993
171.164
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240


OH
OH
O
OAc

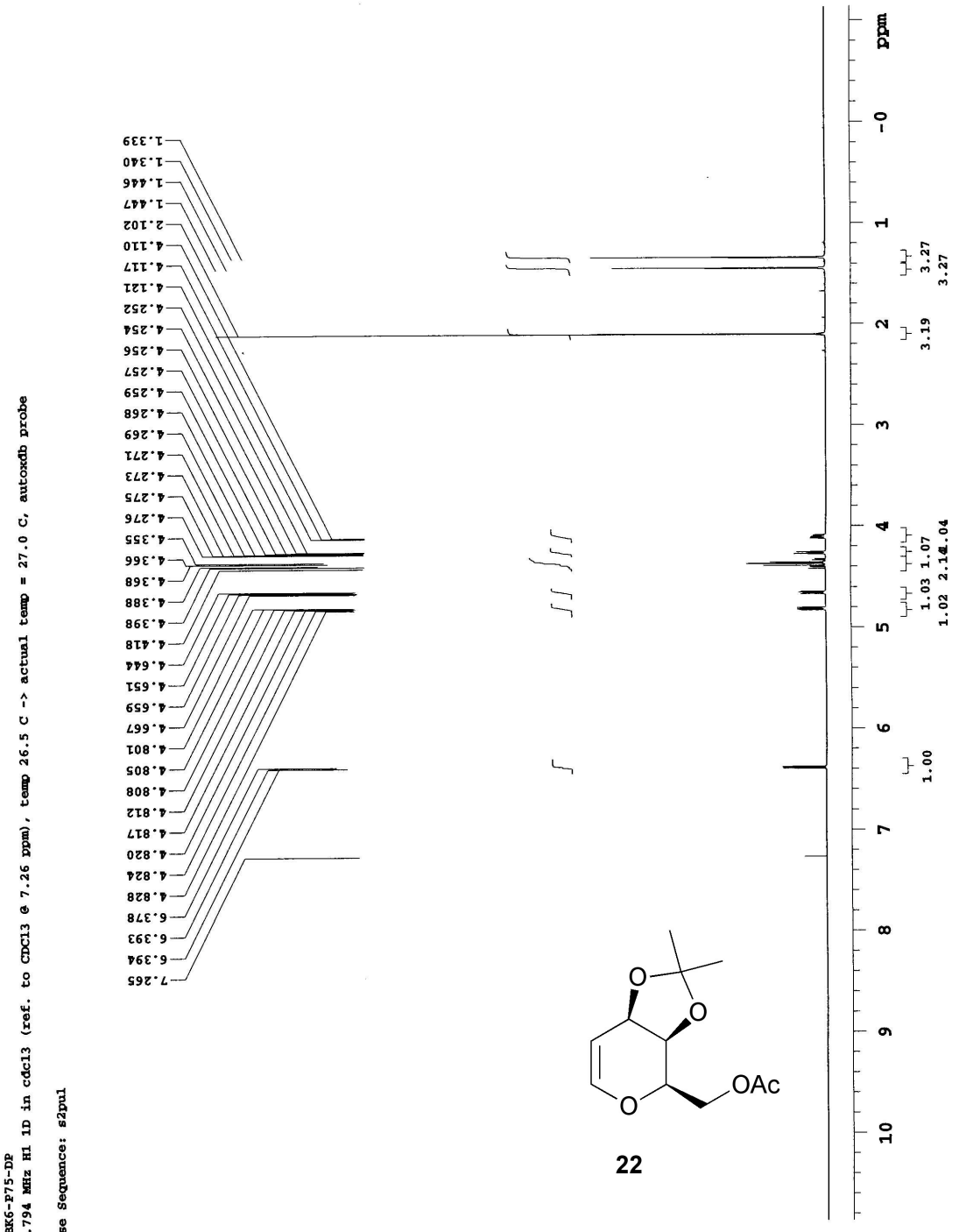
pre-22


RS-BK6-P103
99.794 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe
Pulse Sequence: s2pul
2.115
2.116
2.330
2.352
2.437
2.455
3.919
3.932
4.085
4.101
4.116
4.302
4.320
4.331
4.349
4.404
4.418
4.434
4.447
4.727
4.731
4.736
4.742
4.747
4.752
6.389
6.393
6.405
6.409
7.264
7.265
1.00
2.151.10
1.03 1.06 1.05
1.003.29
0.94
ppm
OH
OH
OAc
O
pre-22

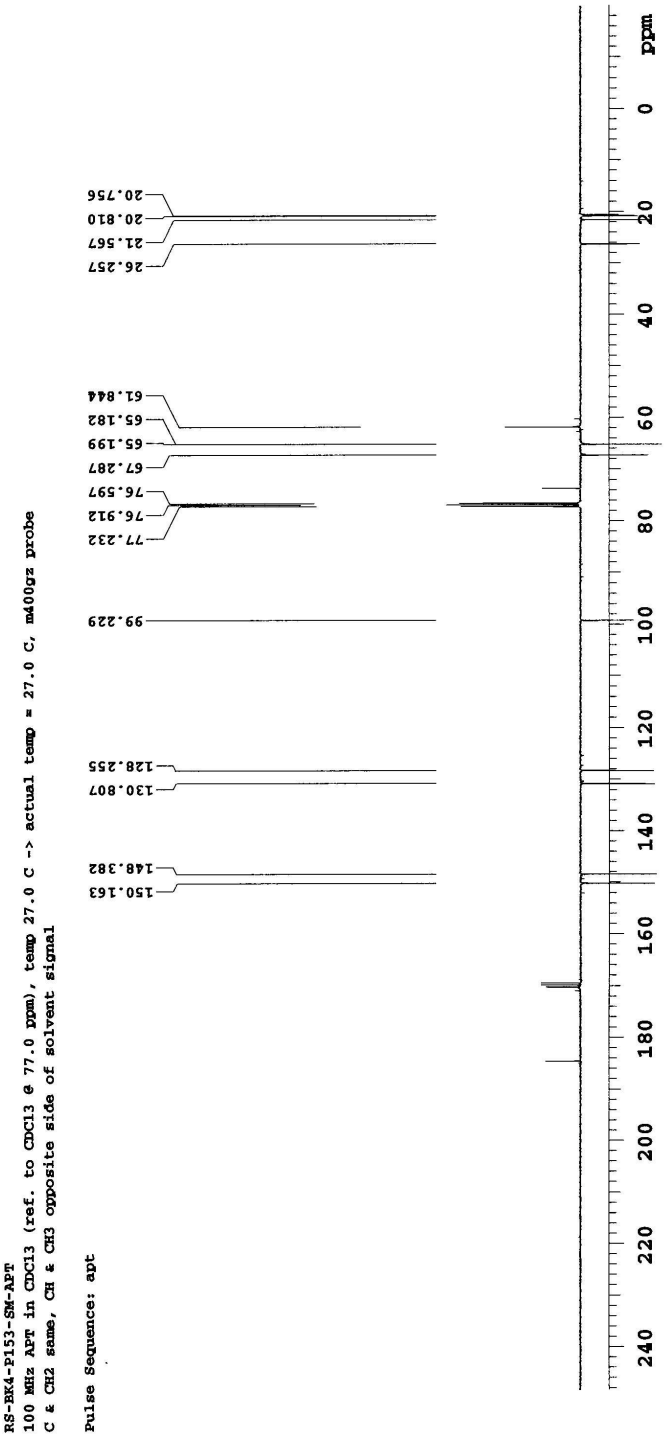

RS-BK6-P75-DP-APT
100.539 MHz C13[H1] apt in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: apt
20.839
26.816
27.946
64.195
68.492
72.461
72.715
76.689
77.008
77.323
102.610
110.737
144.516
170.724
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240

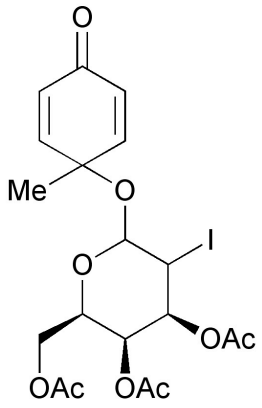

O
O
O
OAc

22

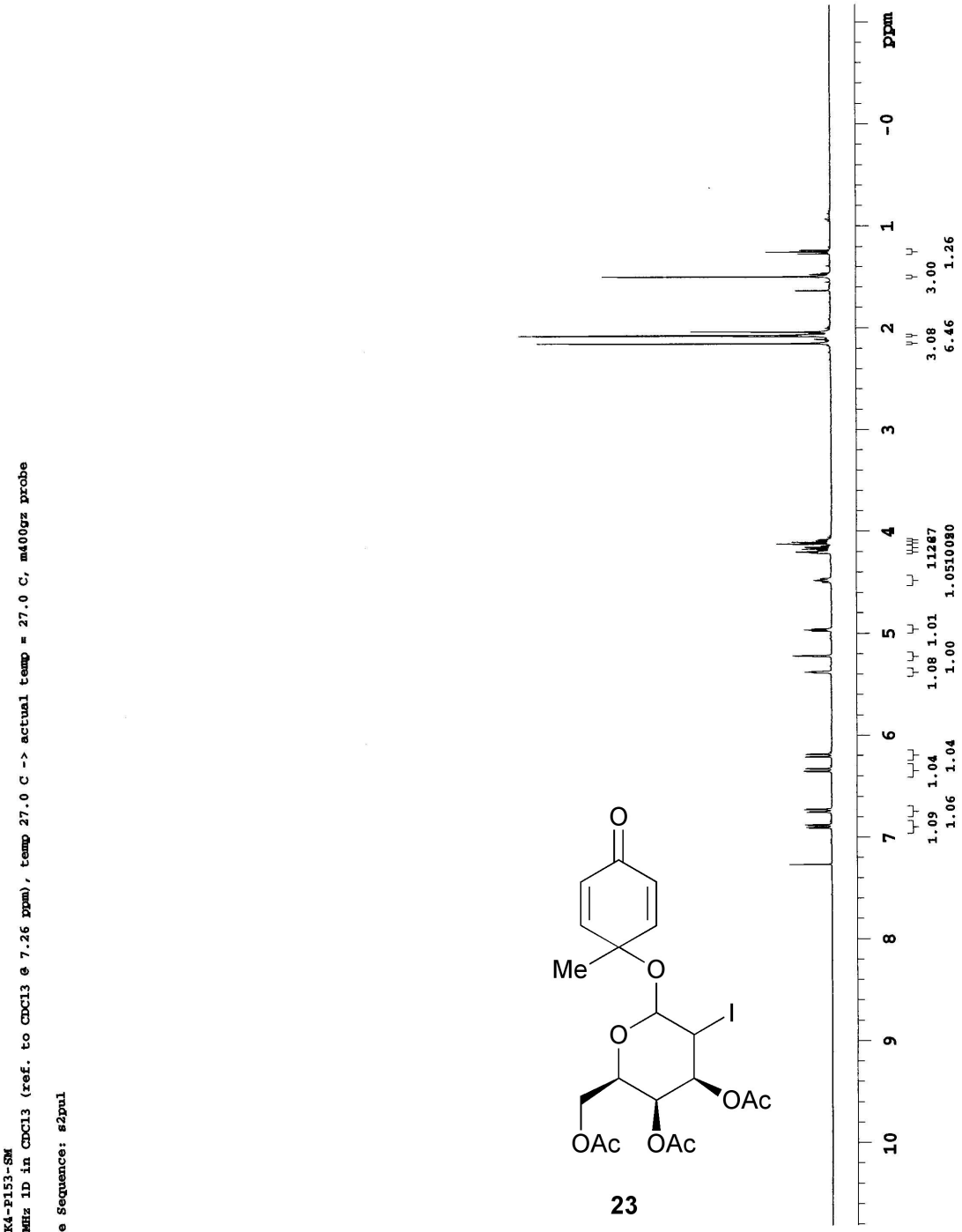

RS-BK6-P75-DP
399.794 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe
Pulse Sequence: s2pul
1.339
1.340
1.446
1.447
2.102
4.110
4.117
4.121
4.252
4.254
4.256
4.257
4.259
4.268
4.269
4.271
4.273
4.275
4.276
4.355
4.366
4.368
4.388
4.398
4.418
4.644
4.651
4.659
4.667
4.801
4.805
4.808
4.812
4.817
4.820
4.824
4.828
6.378
6.393
6.394
7.265
1.00
3.19
3.27
3.27
1.03
1.07
1.02
2.14
4.04
ppm
O
O
O
OAc

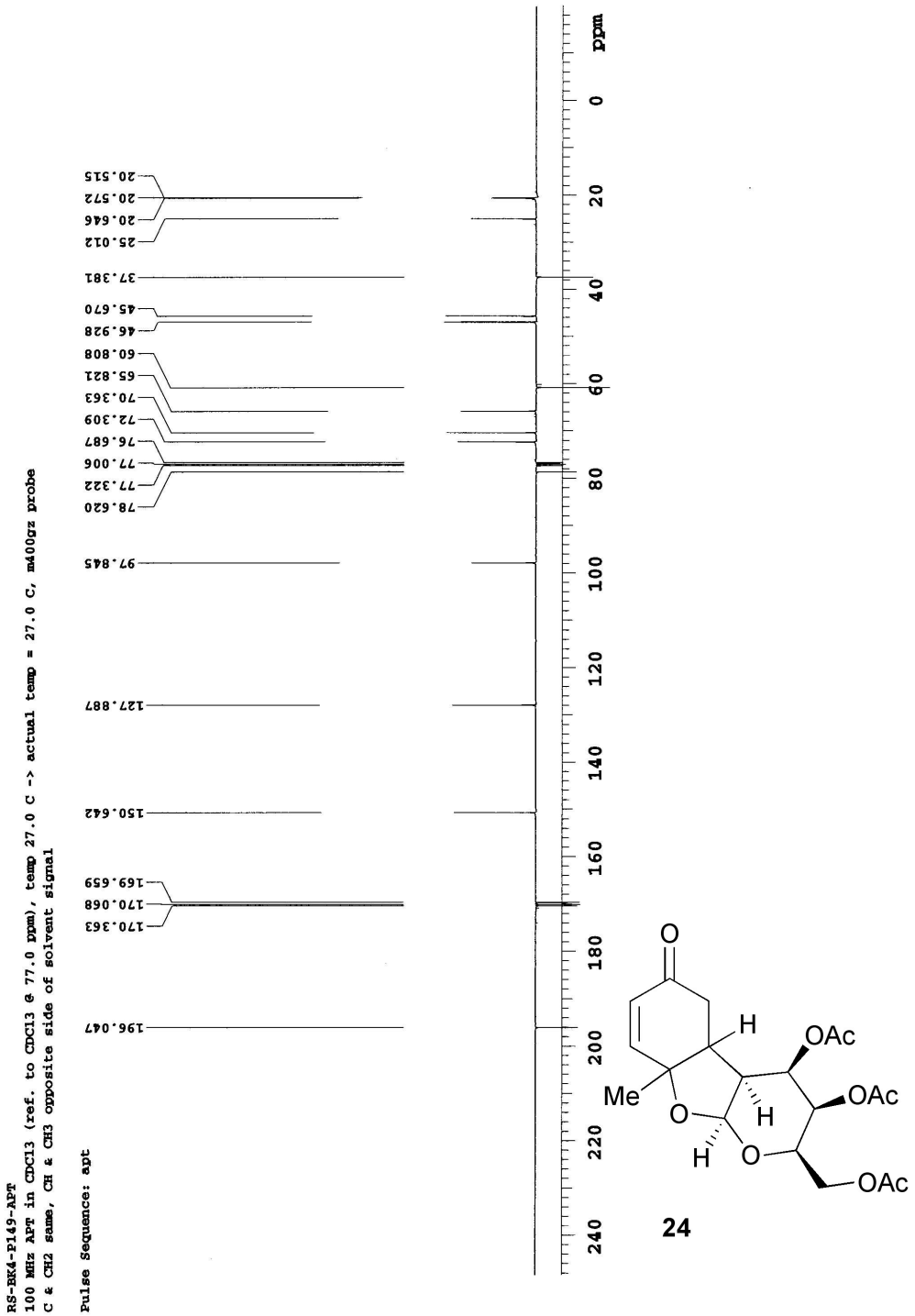
22

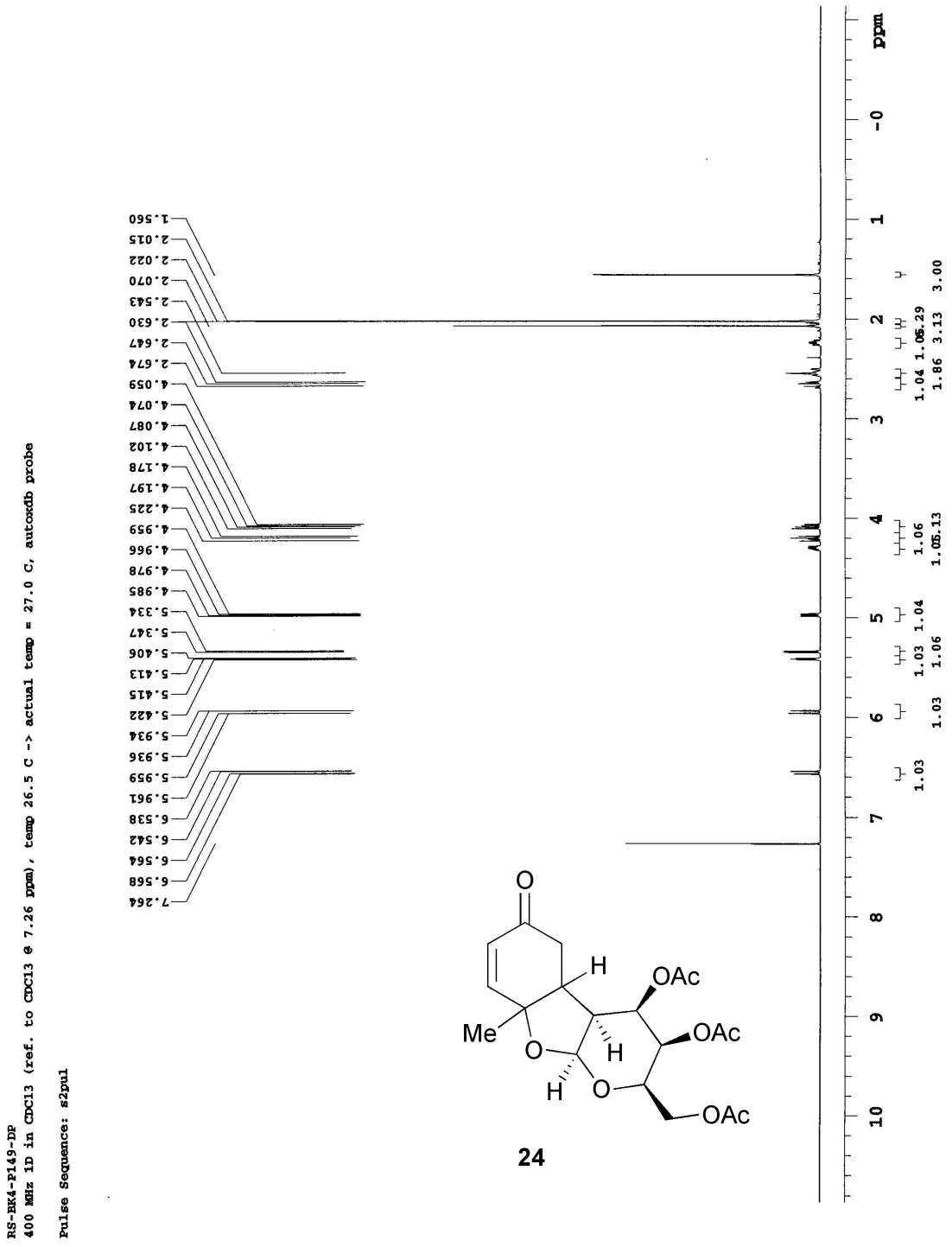

RS-BK4-P153-SM-APT
100 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm), temp 27.0 C -> actual temp = 27.0 C, m400gz probe
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: apt
20.756
20.810
21.567
26.257
61.844
65.182
65.199
67.287
76.597
76.912
77.232
99.229
128.255
130.807
148.382
150.163
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240


O
Me
O
O
I
OAc
OAc
OAc

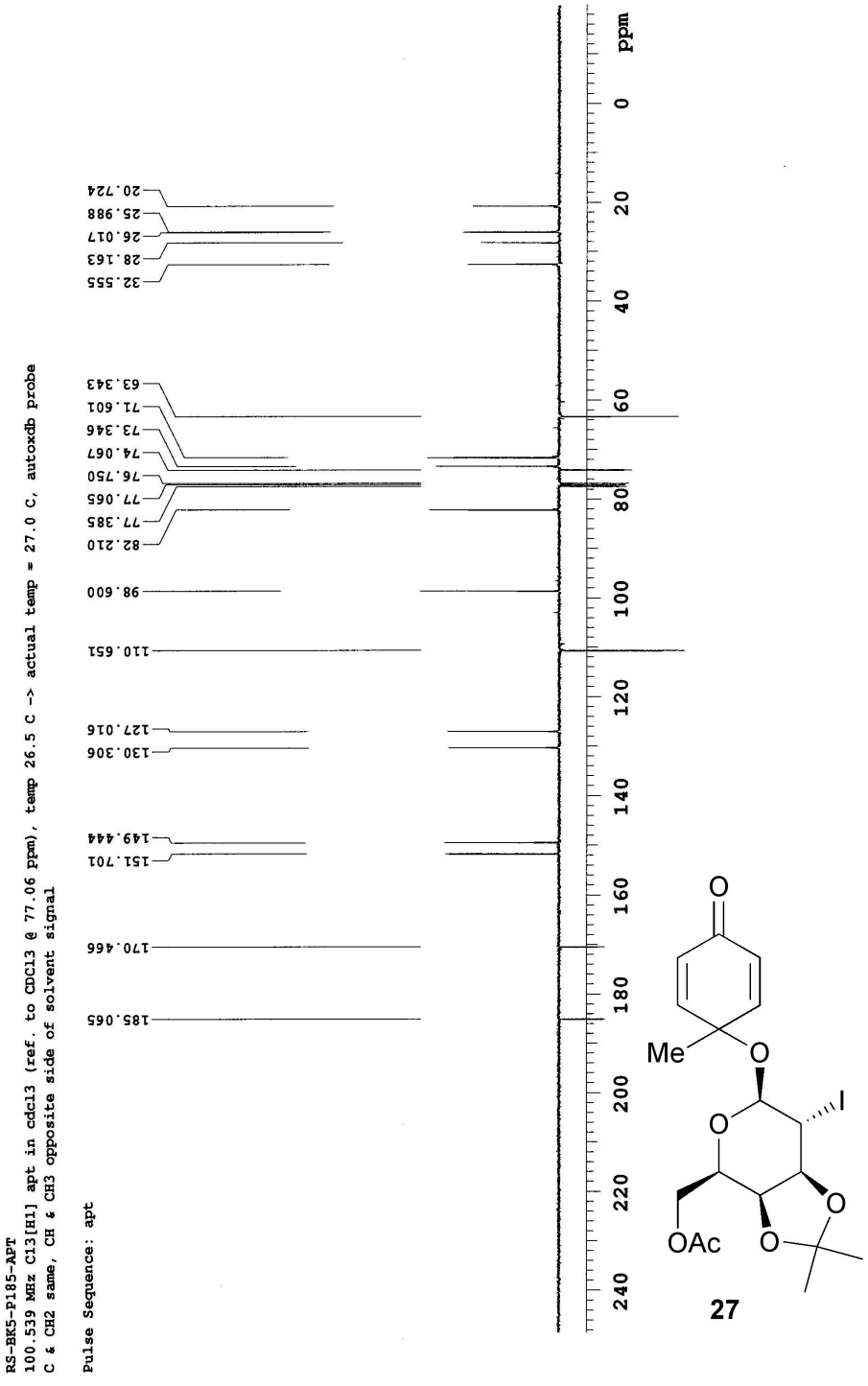
23

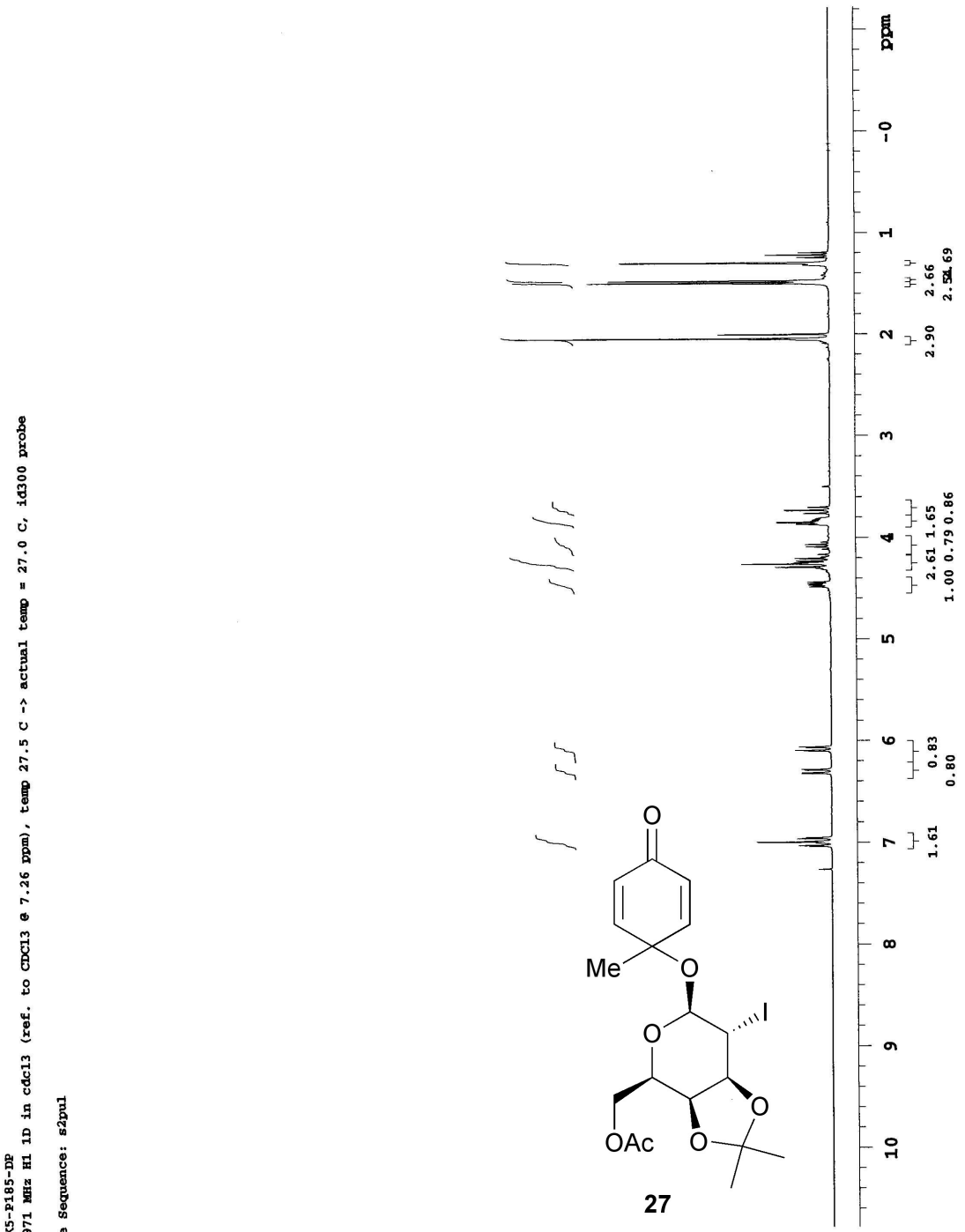

RS-BK4-P153-SM
400 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.0 C -> actual temp = 27.0 C, m400gz probe
Pulse Sequence: s2pul
ppm
Me
O
I
OAc
OAc
OAc
23


RS-BK4-P149-APT
100 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm), temp 27.0 C -> actual temp = 27.0 C, m400gz probe
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: apt
20.515
20.572
20.646
25.012
37.381
45.670
46.928
60.808
65.821
70.363
72.309
76.687
77.006
77.322
78.620
97.845
127.887
150.642
169.659
170.068
170.363
196.047
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
O
H
OAc
Me
O
OAc
H
H
O
OAc
24

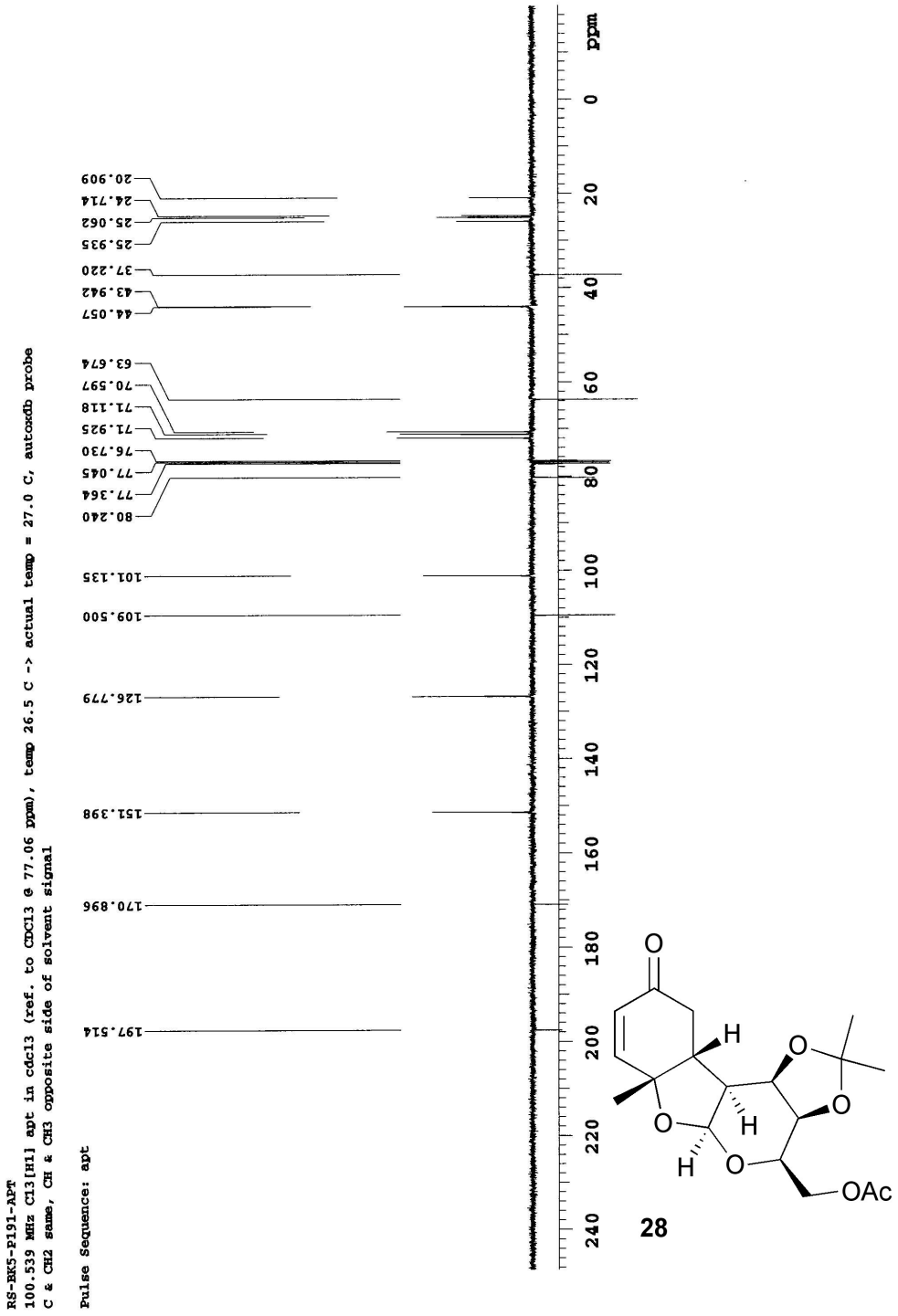

RS-HK4-P149-DP
400 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe
Pulse Sequence: s2pul
7.264
6.568
6.564
6.542
6.538
5.961
5.959
5.936
5.934
5.422
5.415
5.413
5.406
5.347
5.334
4.985
4.978
4.966
4.959
4.225
4.197
4.178
4.102
4.087
4.074
4.059
2.674
2.647
2.630
2.543
2.070
2.022
2.015
1.560
1.03
1.03
1.06
1.04
1.03
1.06
1.05
1.04
1.86
3.13
3.00
ppm
O
H
OAc
Me
O
OAc
H
H
O
OAc

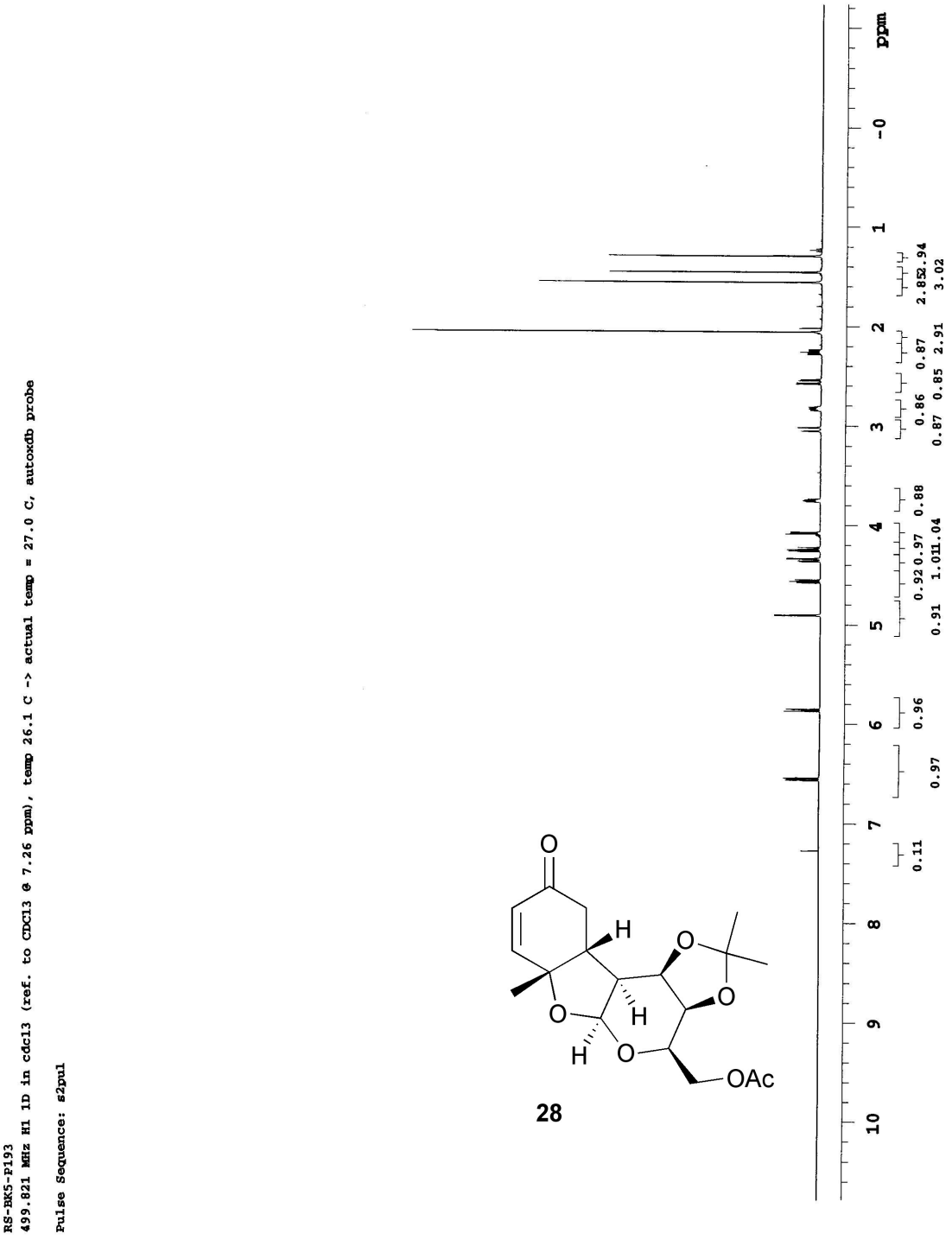
24

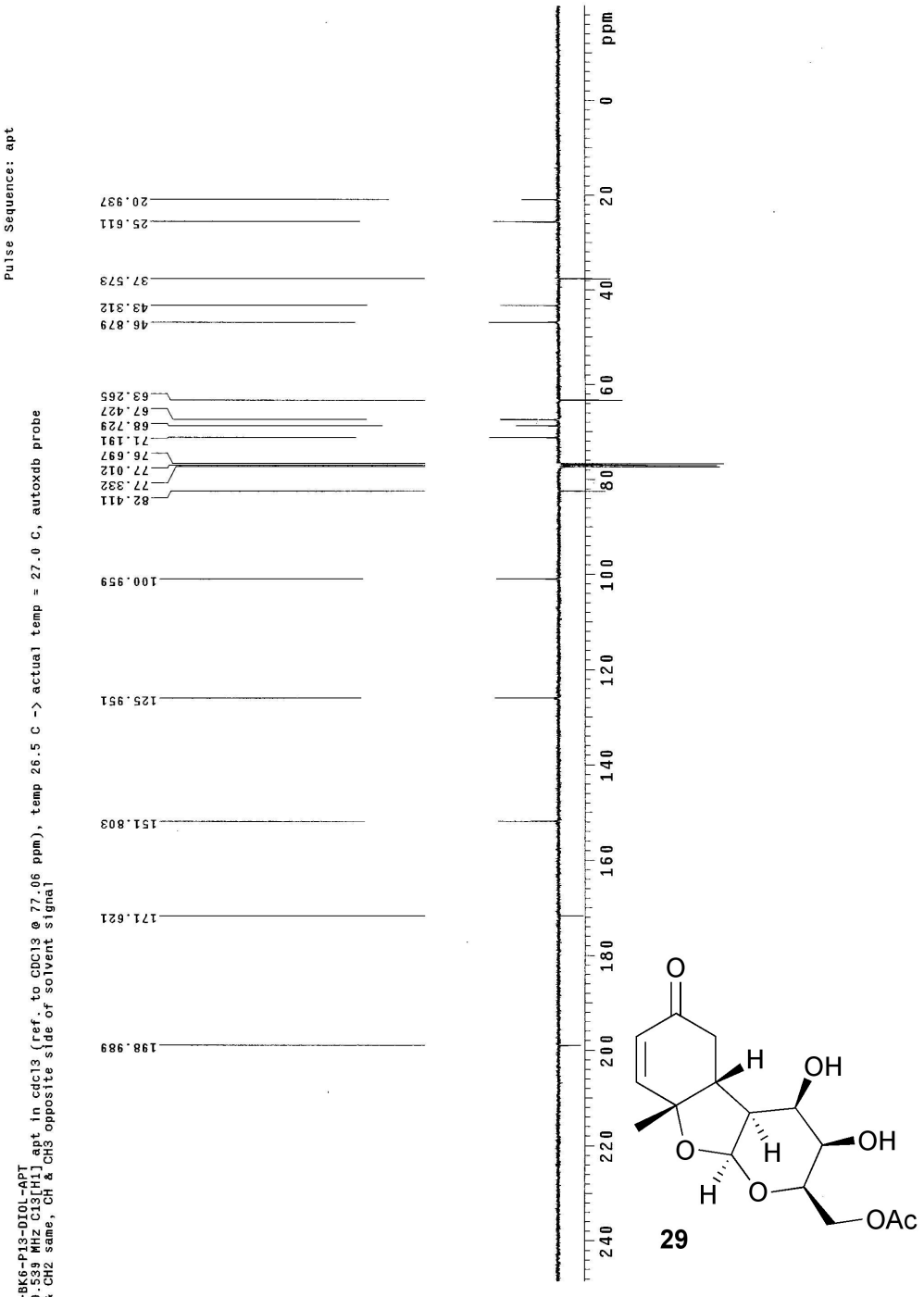

RS-BK5-P185-APT
100.539 MHz C13[H1] apt in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: apt
20.724
25.988
26.017
28.163
32.555
63.343
71.601
73.346
74.067
76.750
77.065
77.385
82.210
98.600
110.651
127.016
130.306
149.444
151.701
170.466
185.065
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
O
Me
O
O
I
O
OAc
O
27

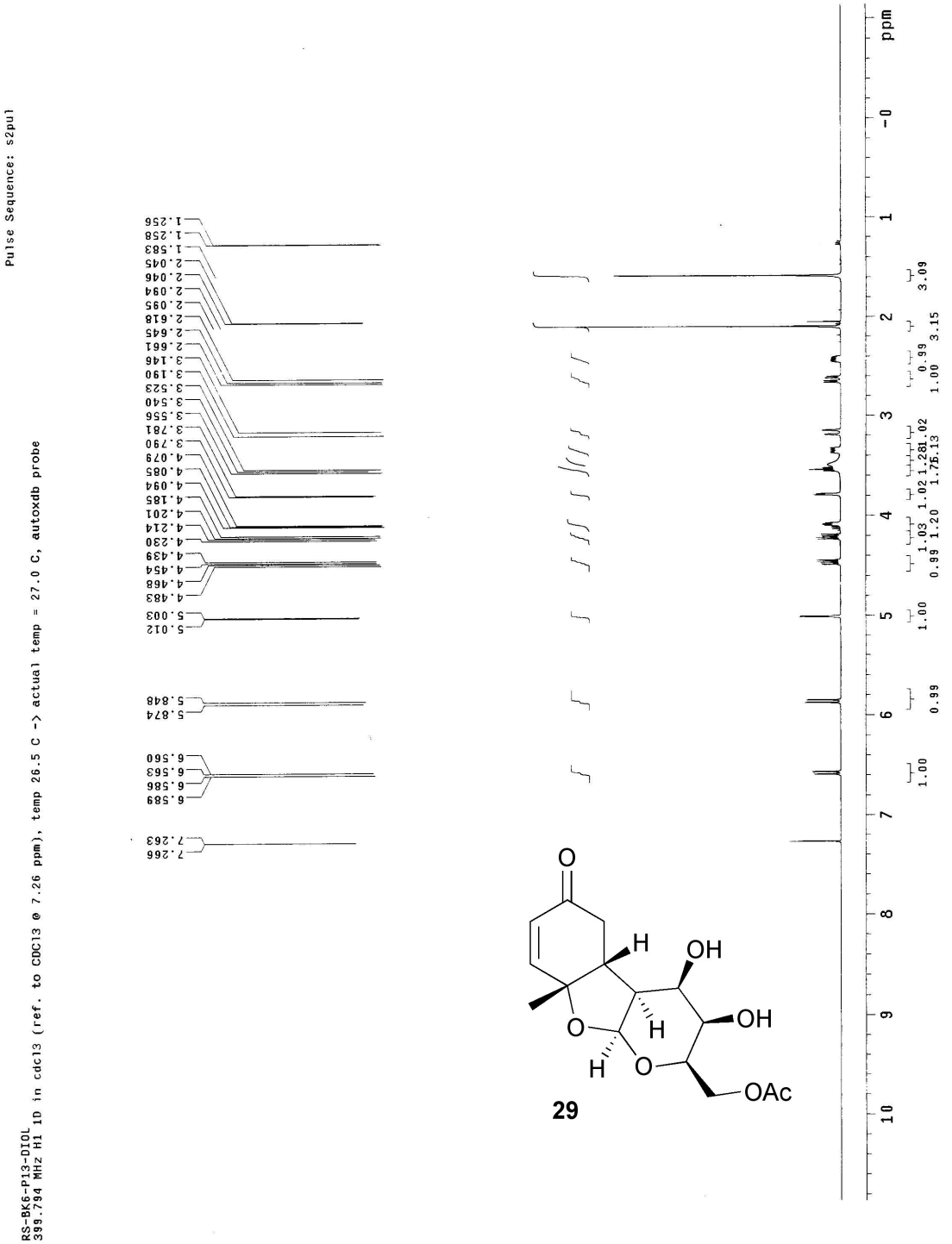

RS-RK5-P185-DP
299.971 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.5 C -> actual temp = 27.0 C, id300 probe
Pulse Sequence: s2pul
ppm
1.61
0.83
0.80
2.61 1.65
1.00 0.79 0.86
2.90
2.66
2.54 2.69
Me
O
O
I
O
O
OAc
O

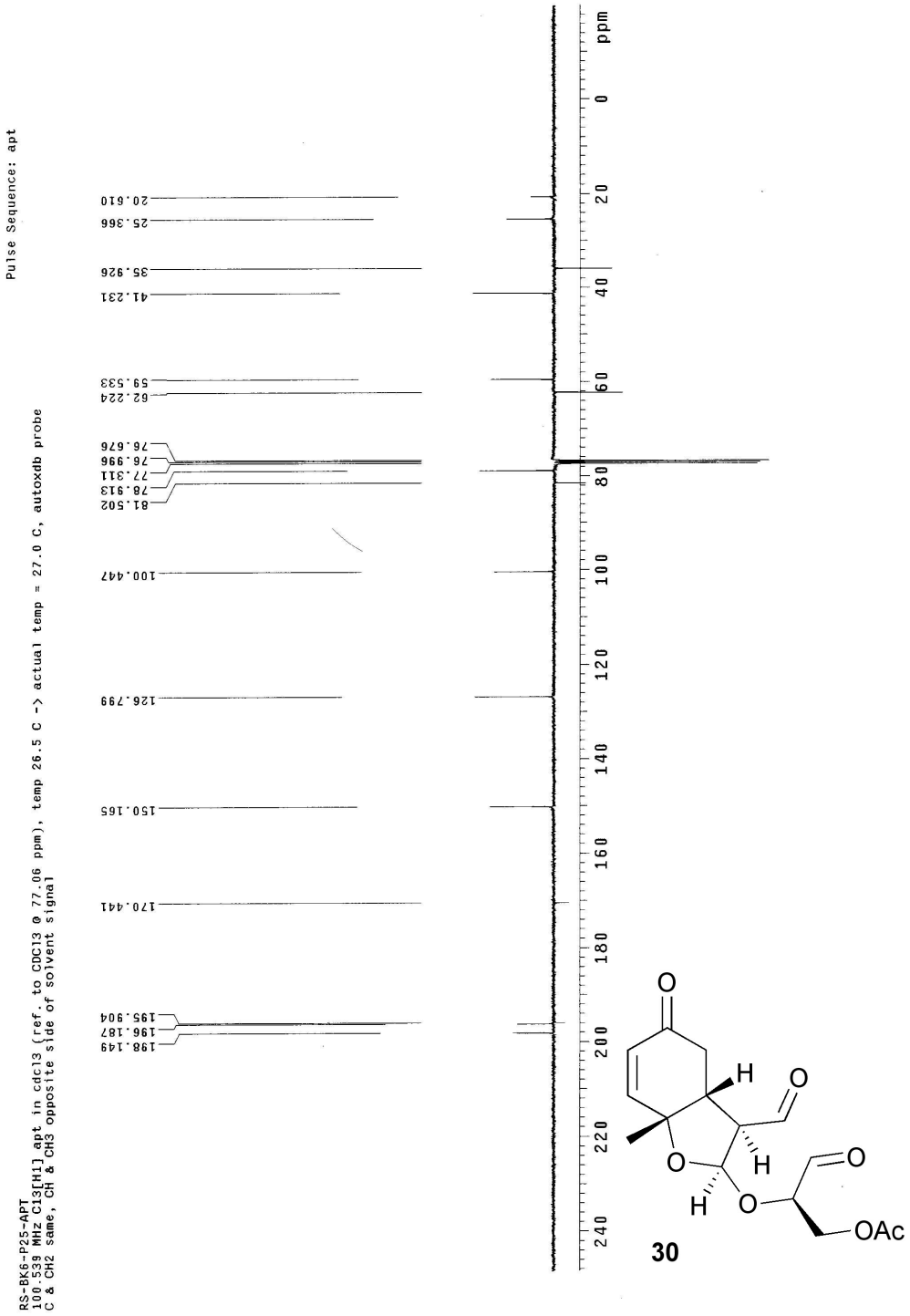
27

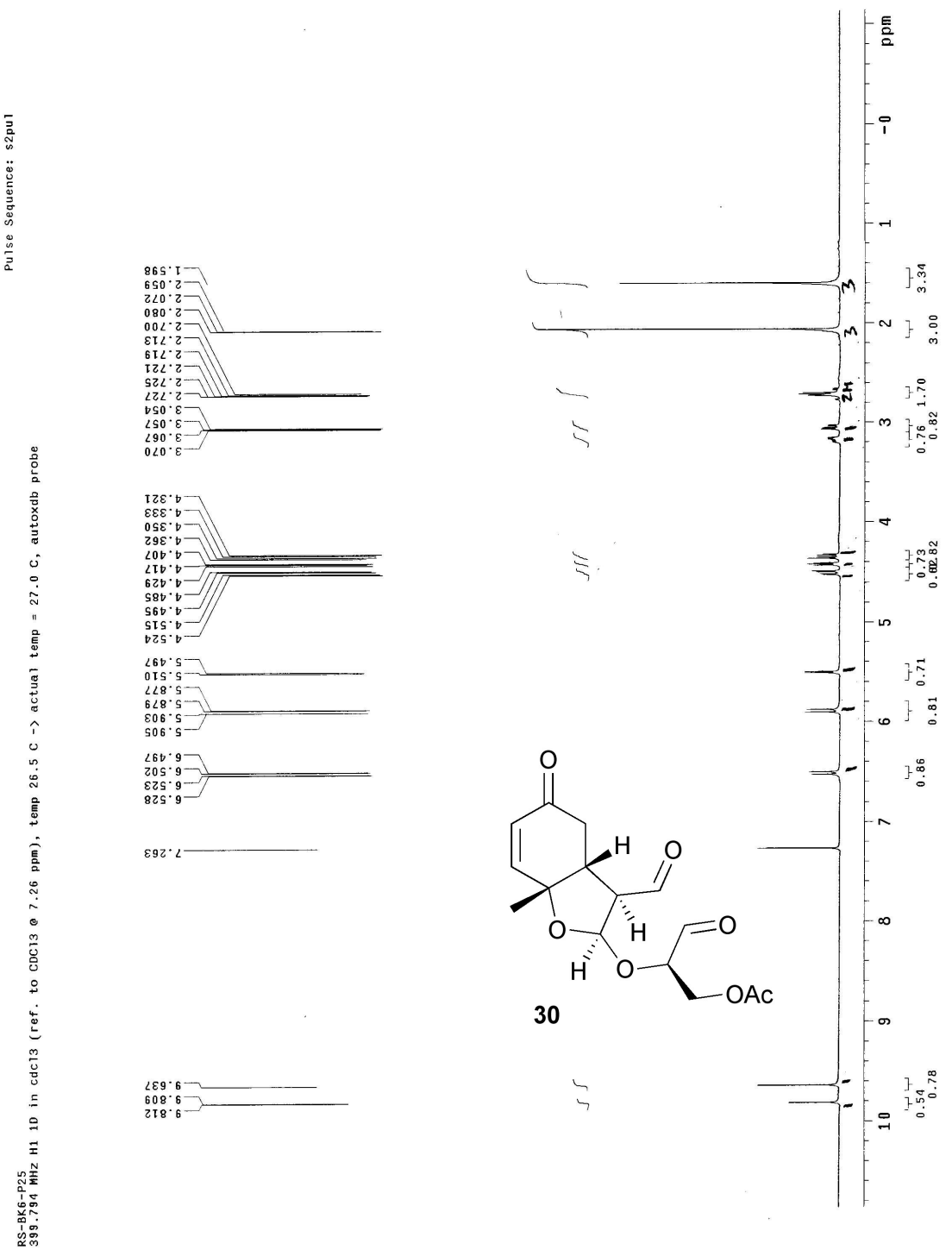

RS-BK5-P191-APT
100.539 MHz C13[H1] apt in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: apt
20.909
24.714
25.062
25.935
37.220
43.942
44.057
63.674
70.597
71.118
71.925
76.730
77.045
77.364
80.240
101.135
109.500
126.779
151.398
170.896
197.514
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
O
H
O
O
O
H
H
O
OAc
28

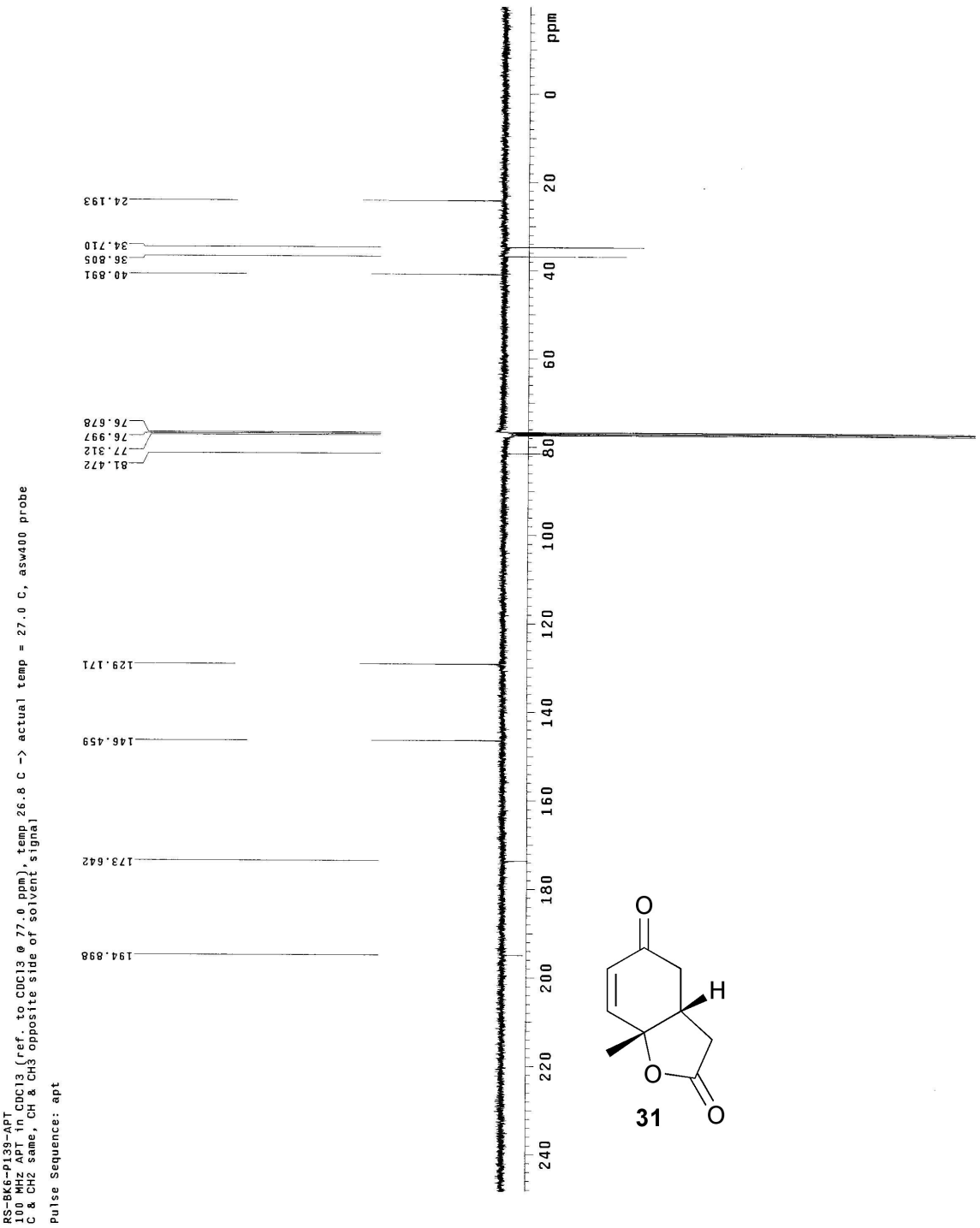

RS-BK5-P193
499.821 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxdb probe
Pulse Sequence: s2pul
ppm
0.11
0.97
0.96
0.91
0.92
0.97
1.01
1.04
0.88
0.87
0.86
0.85
0.87
2.91
2.85
2.94
3.02
O
H
O
O
H
O
H
O
OAc
28

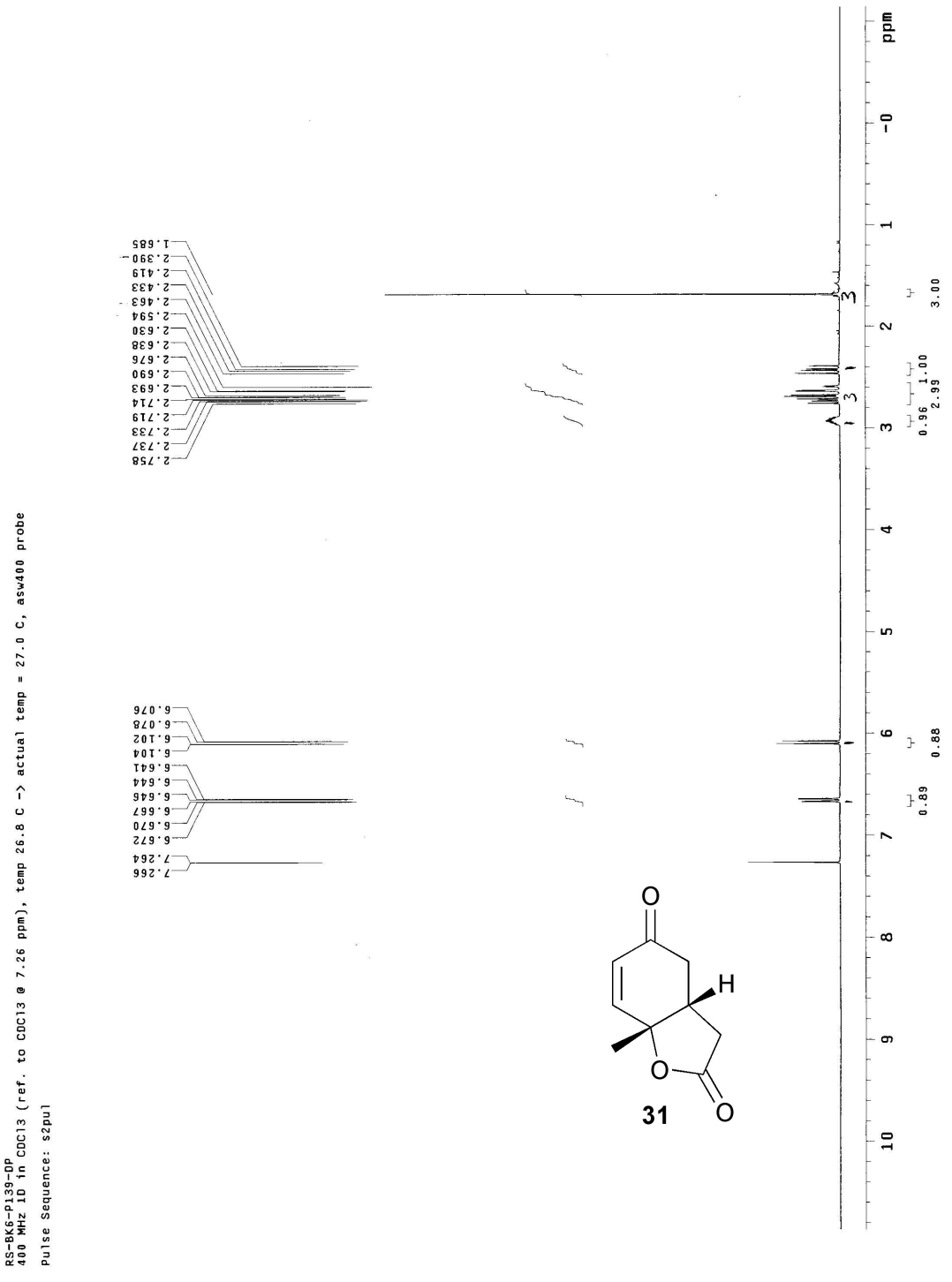

Pulse Sequence: apt
RS-BK6-P13-DIOL-APT
100.539 MHz C13[H1] apt in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal
20.937
25.611
37.573
43.312
46.879
63.265
67.427
68.729
71.191
76.697
77.012
77.332
82.411
100.959
125.951
151.803
171.621
198.989
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
O
H
OH
O
H
OH
H
O
OAc
29

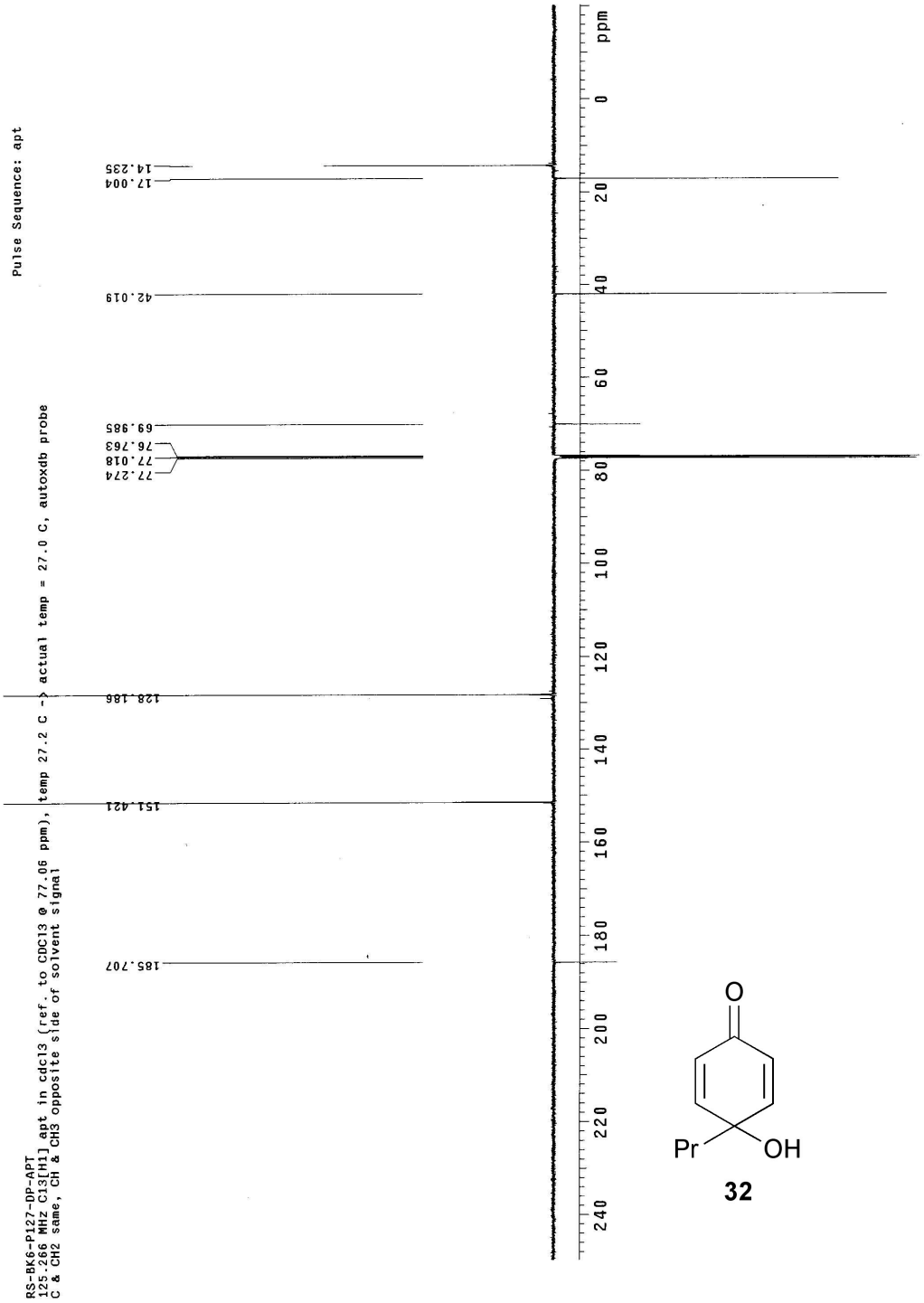

Pulse Sequence: s2pul
RS-BK6-P13-DIOL
399.794 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe
1.256
1.258
1.583
2.045
2.046
2.094
2.095
2.618
2.645
2.661
3.146
3.190
3.523
3.540
3.556
3.781
3.790
4.079
4.085
4.094
4.185
4.201
4.214
4.230
4.439
4.454
4.468
4.483
5.003
5.012
5.848
5.874
6.560
6.563
6.586
6.589
7.263
7.266
1.00
0.99
1.00
0.99
1.03
1.20
1.02
1.78
1.02
1.13
0.99
1.00
3.09
3.15
ppm
O
H
OH
O
H
OH
H
O
OAc
29


Pulse Sequence: apt
RS-BK6-P25-APT
100.539 MHz C13[H1] apt in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal
20.610
25.366
35.926
41.231
59.533
62.224
76.676
76.996
77.311
78.913
81.502
100.447
126.799
150.165
170.441
195.904
196.187
198.149
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
O
H
O
O
H
H
O
O
OAc
30

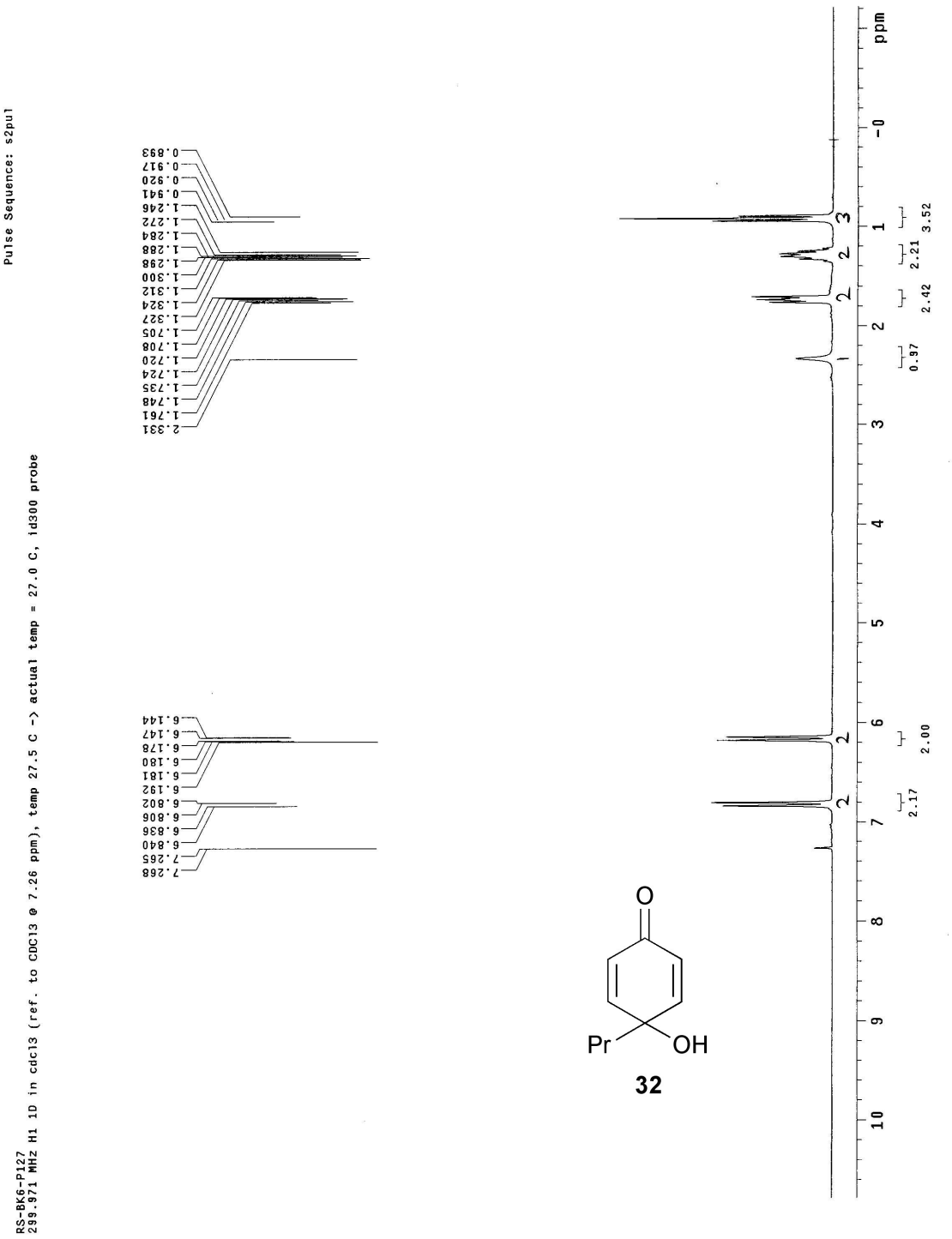

Pulse Sequence: s2pul
RS-BK6-P25
399.794 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe
1.598
2.059
2.072
2.080
2.700
2.713
2.719
2.721
2.725
2.727
3.054
3.057
3.067
3.070
4.321
4.333
4.350
4.362
4.407
4.417
4.429
4.485
4.495
4.515
4.524
5.497
5.510
5.877
5.879
5.903
5.905
6.497
6.502
6.523
6.528
7.263
9.637
9.809
9.812
ppm
O
H
O
O
H
O
H
O
OAc
30

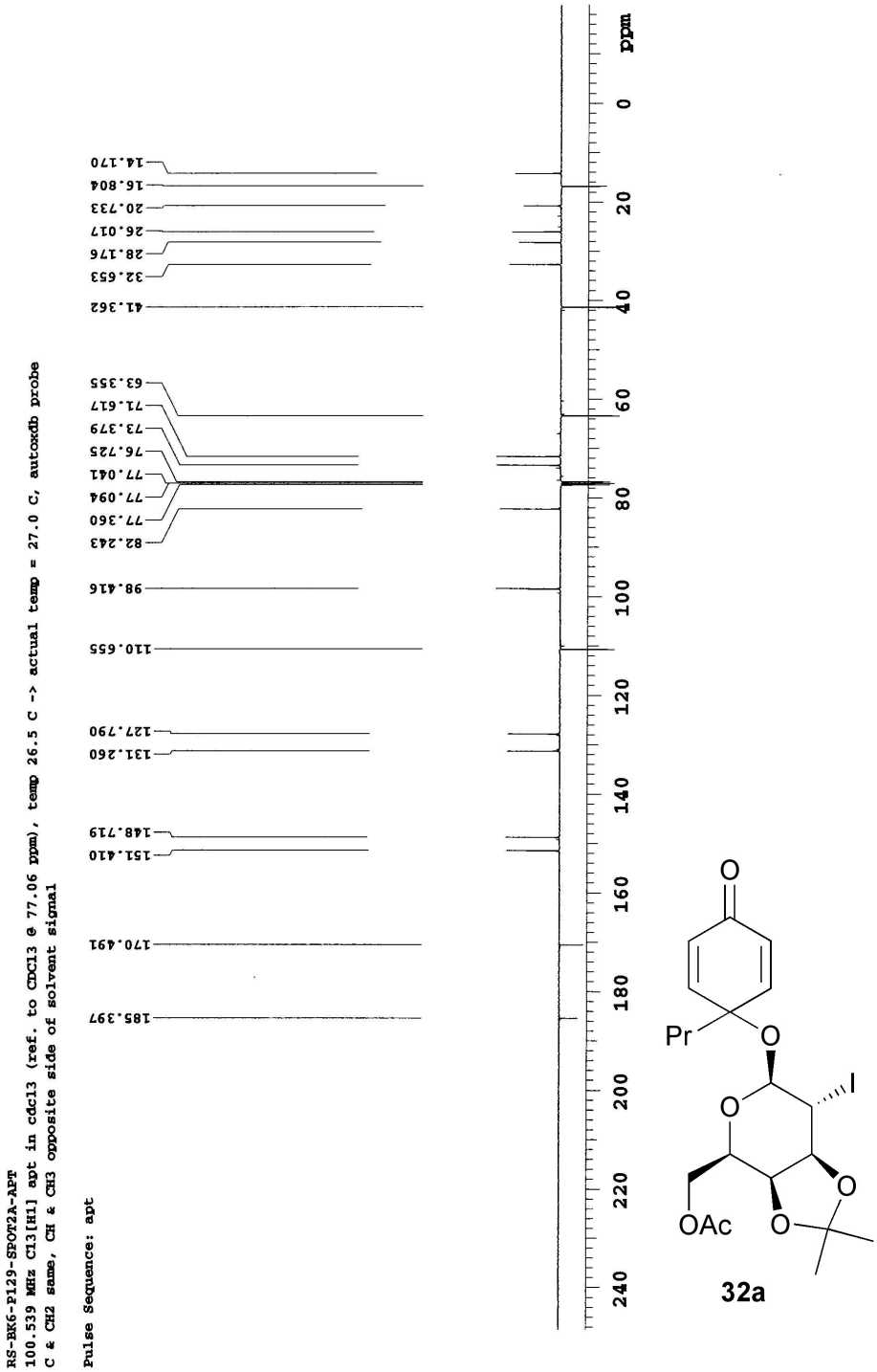

RS-BK6-P139-APT
100 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm), temp 26.8 C -> actual temp = 27.0 C, asw400 probe
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: apt
24.193
34.710
36.805
40.891
76.678
76.997
77.312
81.472
129.171
146.459
173.642
194.898
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
O
H
O
O
31


RS-BK6-P139-DP
400 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 26.8 C -> actual temp = 27.0 C, asw400 probe
Pulse Sequence: s2pul
ppm
31

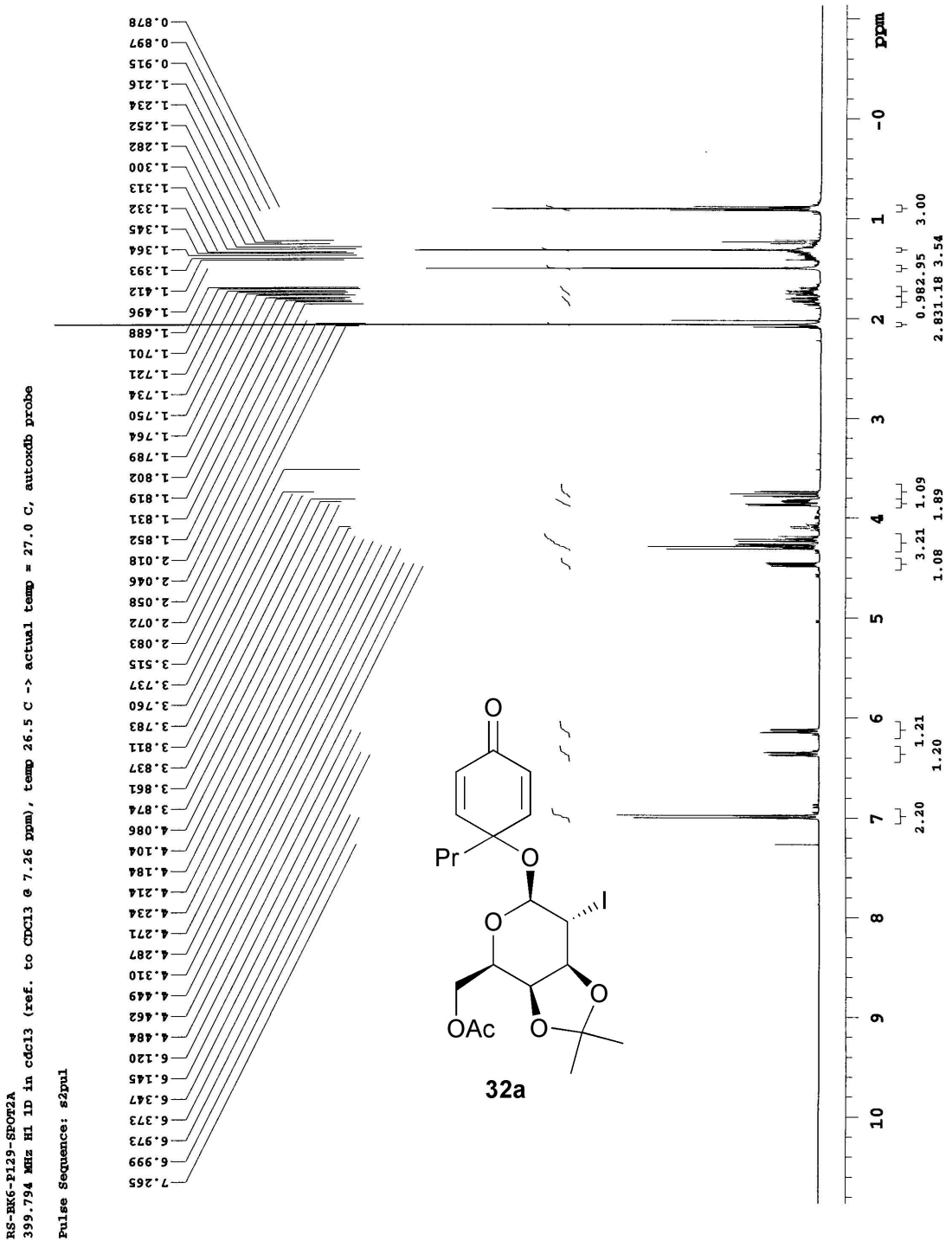

Pulse Sequence: apt
RS-BK6-P127-DP-APT
125.266 MHz C13{H1} apt in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.2 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal
14.235
17.004
42.019
69.985
76.763
77.018
77.274
128.186
151.421
185.707
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
O
Pr
OH

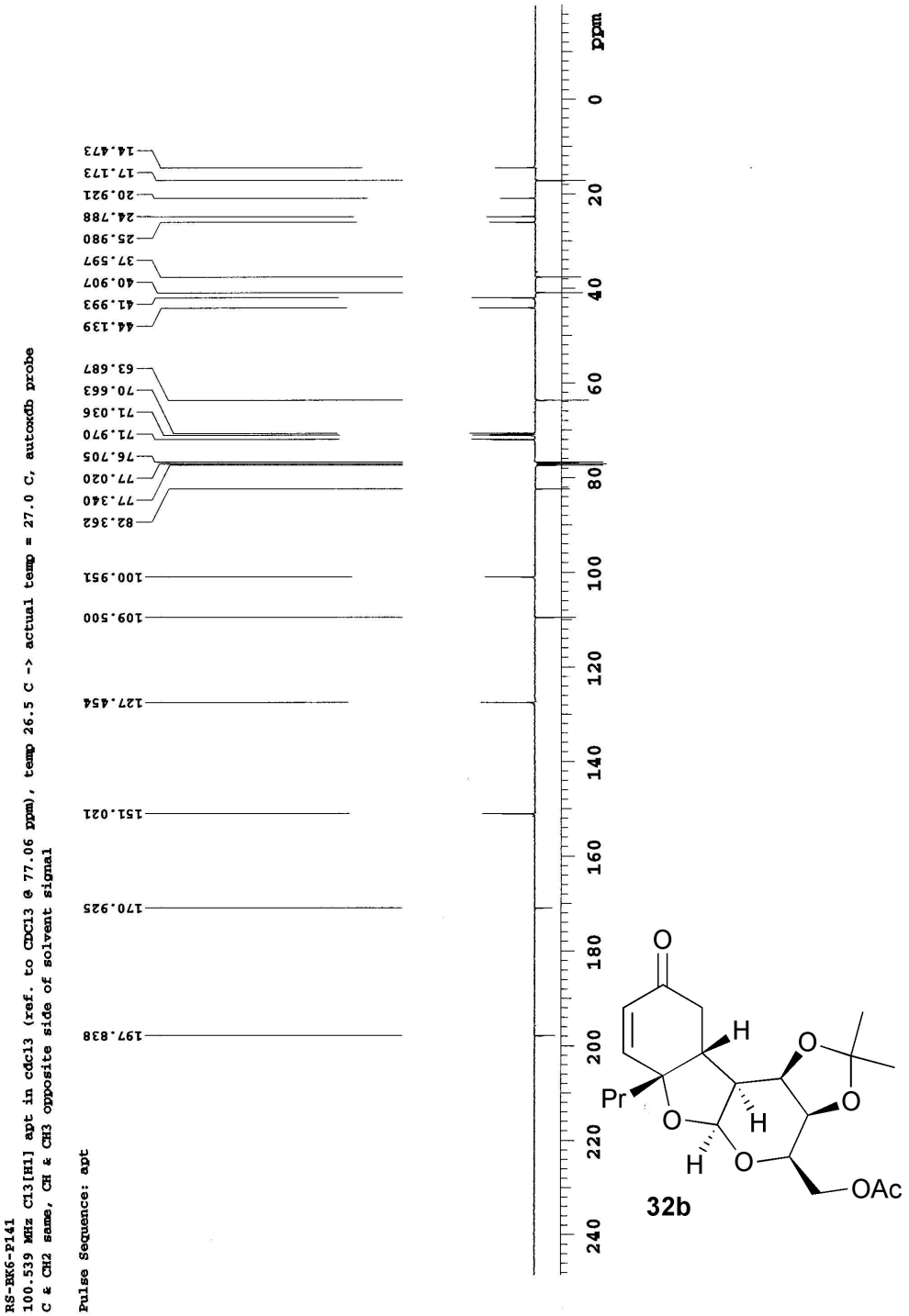
32

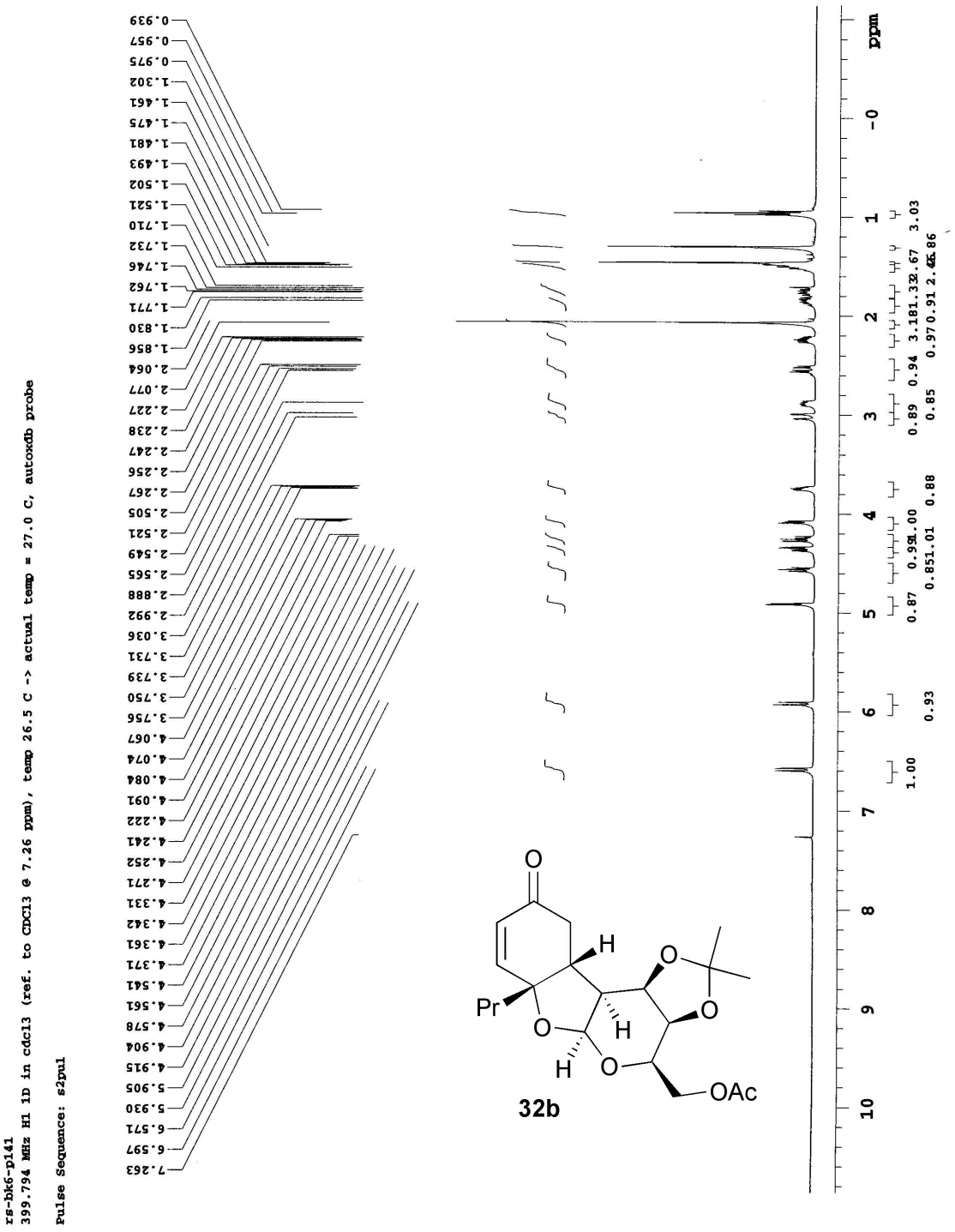

Pulse Sequence: s2pul
RS-BK6-P127
299.971 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.5 C -> actual temp = 27.0 C, id300 probe
0.893
0.917
0.920
0.941
1.246
1.272
1.284
1.288
1.298
1.300
1.312
1.324
1.327
1.705
1.708
1.720
1.724
1.735
1.748
1.761
2.331
6.144
6.147
6.178
6.180
6.181
6.192
6.802
6.806
6.836
6.840
7.265
7.268
ppm
0.97
2.42
2.21
3.52
2.17
2.00
O
Pr
OH
32

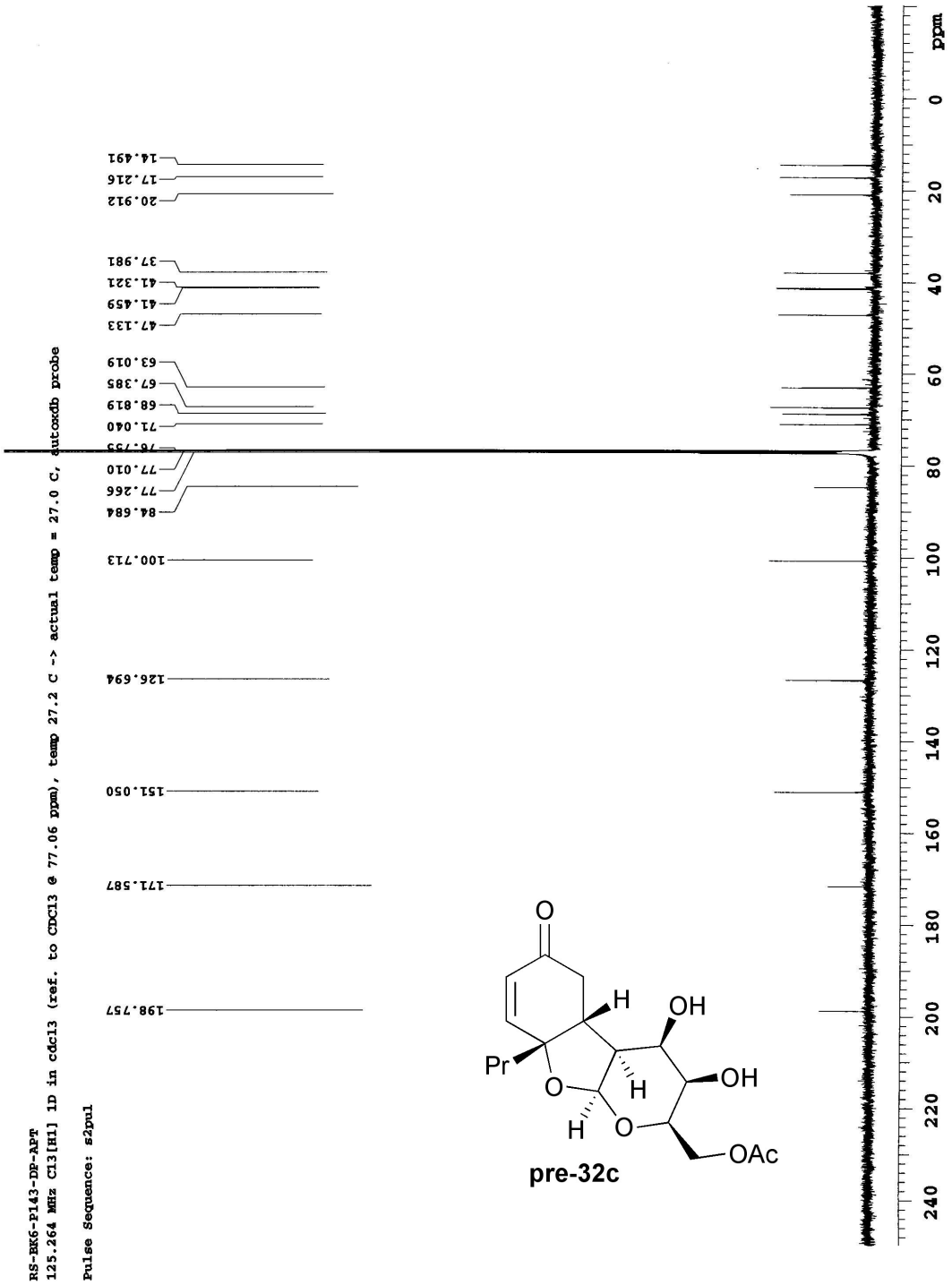

RS-BK6-P129-SPOT2A-APT
100.539 MHz C13[H1] apt in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 26.5 C -> actual temp = 27.0 C, autosdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: apt
14.170
16.804
20.733
26.017
28.176
32.653
41.362
63.355
71.617
73.379
76.725
77.041
77.094
77.360
82.243
98.416
110.655
127.790
131.260
148.719
151.410
170.491
185.397
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
O
Pr
O
O
I
O
OAc
O

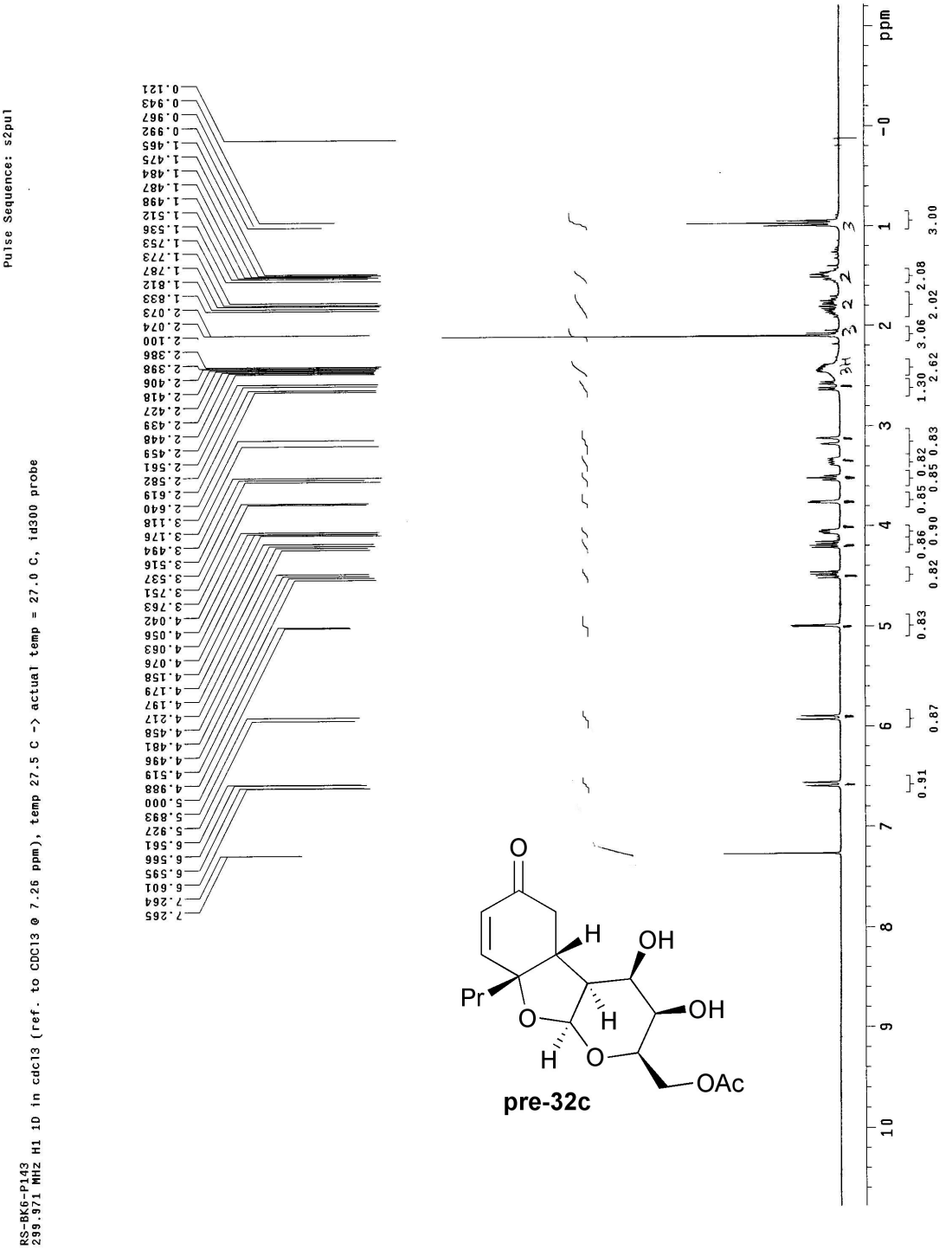
32a

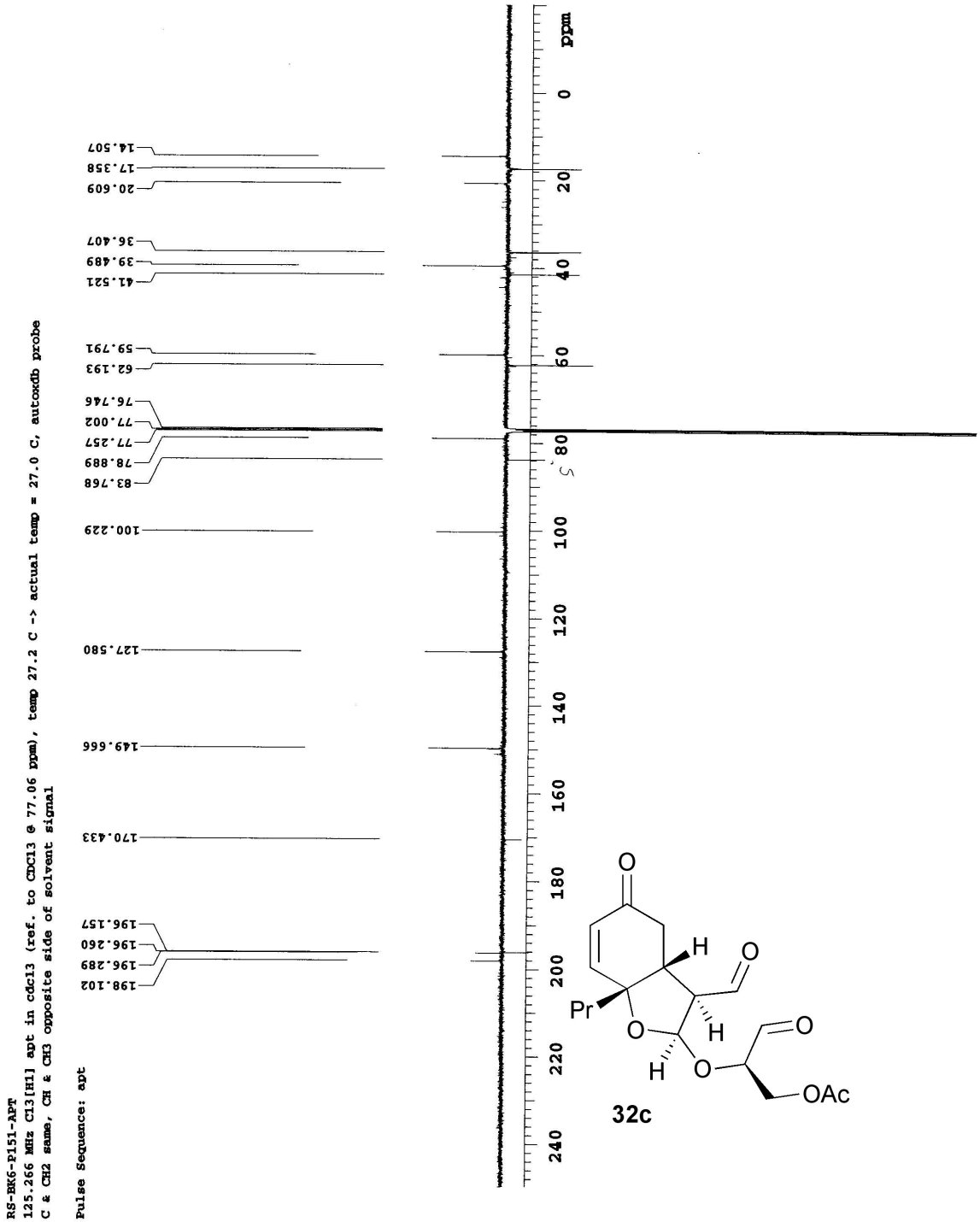

RS-BK6-P129-SPOT2A
399.794 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe
Pulse Sequence: s2pul
ppm
Pr
OAc
32a

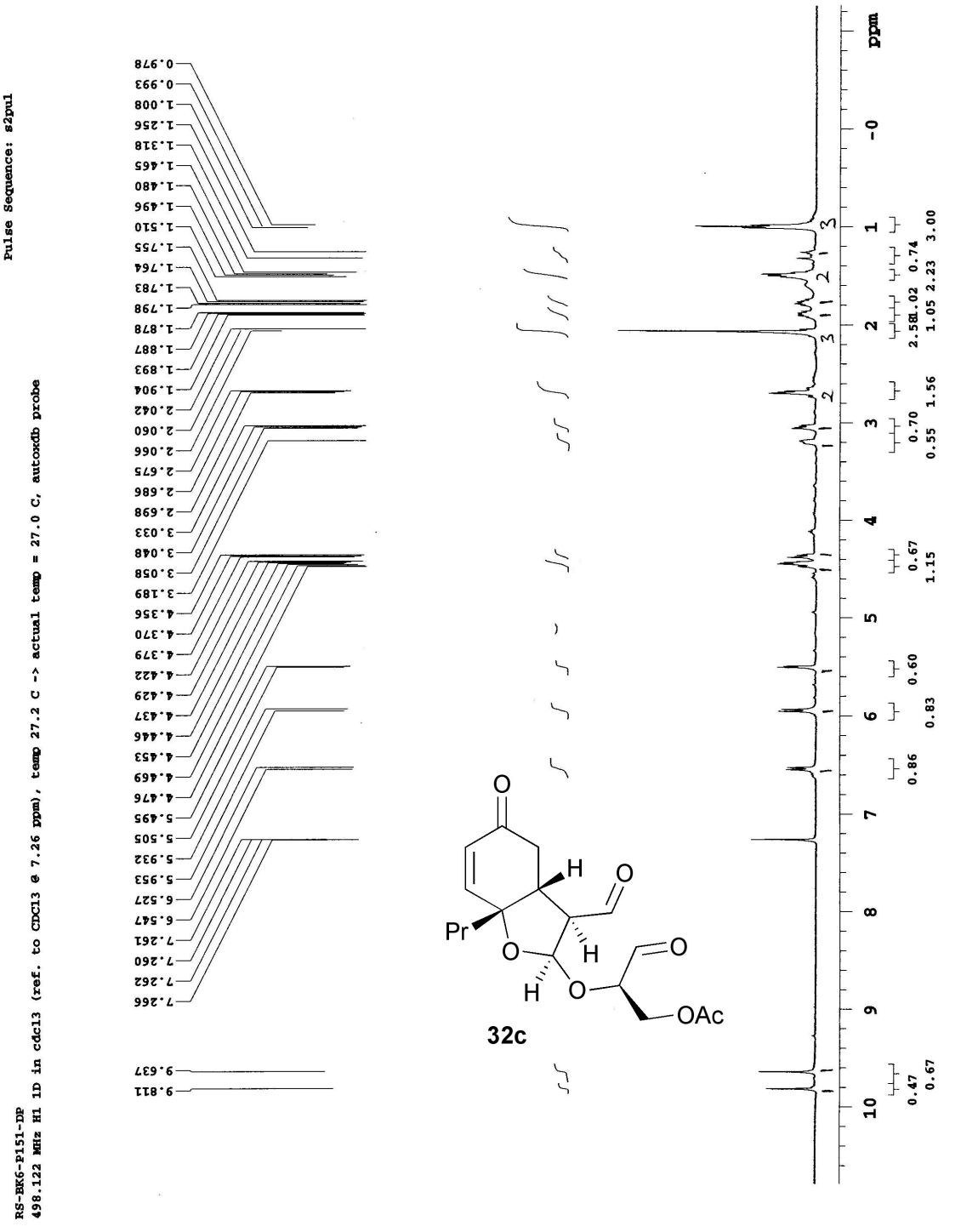

RS-BK6-P141
100.539 MHz C13[H1] apt in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: apt
14.473
17.173
20.921
24.788
25.980
37.597
40.907
41.993
44.139
63.687
70.663
71.036
71.970
76.705
77.020
77.340
82.362
100.951
109.500
127.454
151.021
170.925
197.838
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
O
H
Pr
O
O
O
H
H
O
OAc
32b

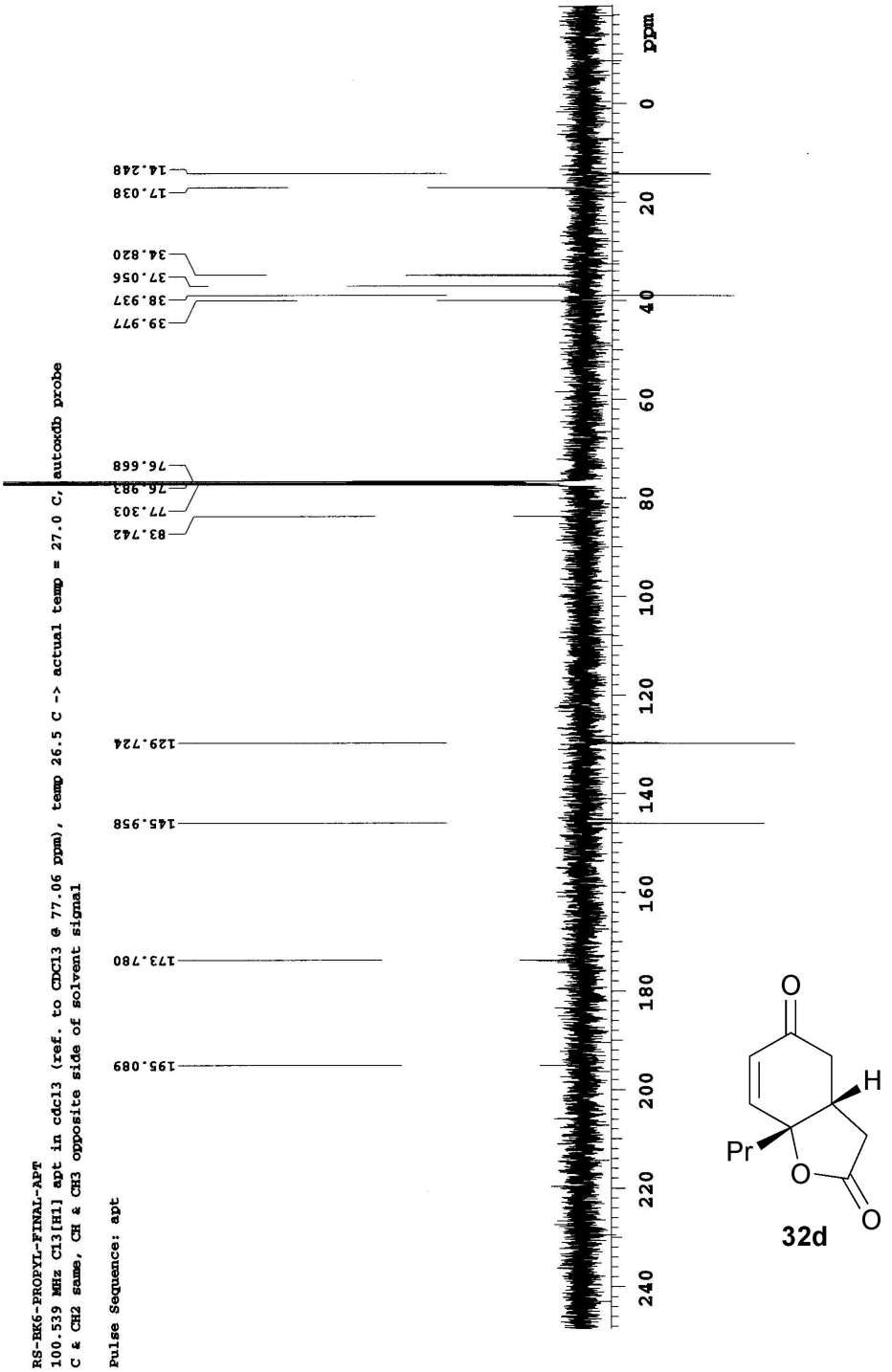

rs-bk6-p141
399.794 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe
Pulse Sequence: s2pul
ppm
Pr
OAc
32b

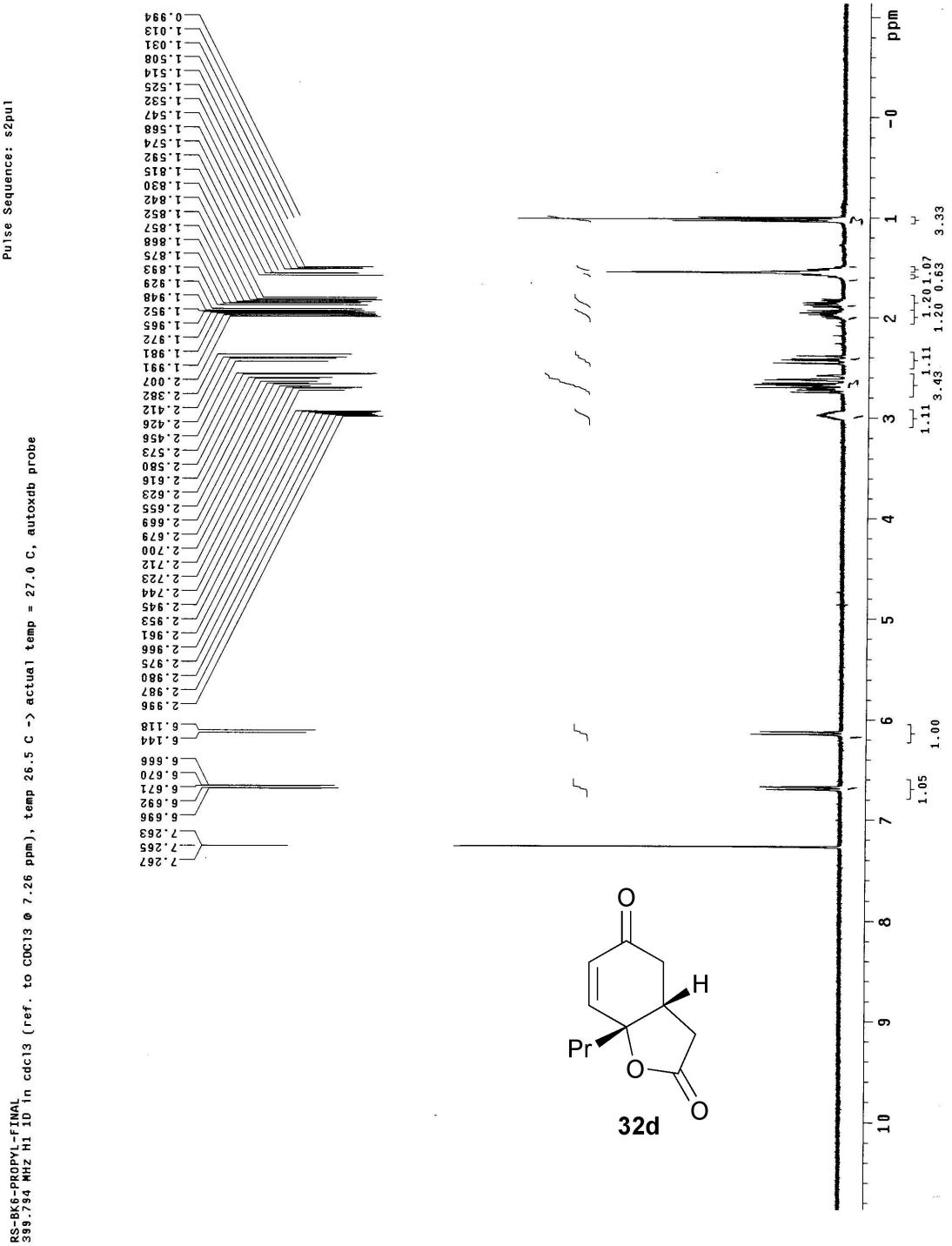

RS-BK6-P143-DP-APT
125.264 MHz C13[H1] 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.2 C -> actual temp = 27.0 C, dutoxdb probe
Pulse Sequence: s2pul
14.491
17.216
20.912
37.981
41.321
41.459
47.133
63.019
67.385
68.819
71.040
76.755
77.010
77.266
84.684
100.713
126.694
151.050
171.587
198.757
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
O
H
OH
Pr
O
H
OH
H
O
OAc
pre-32c

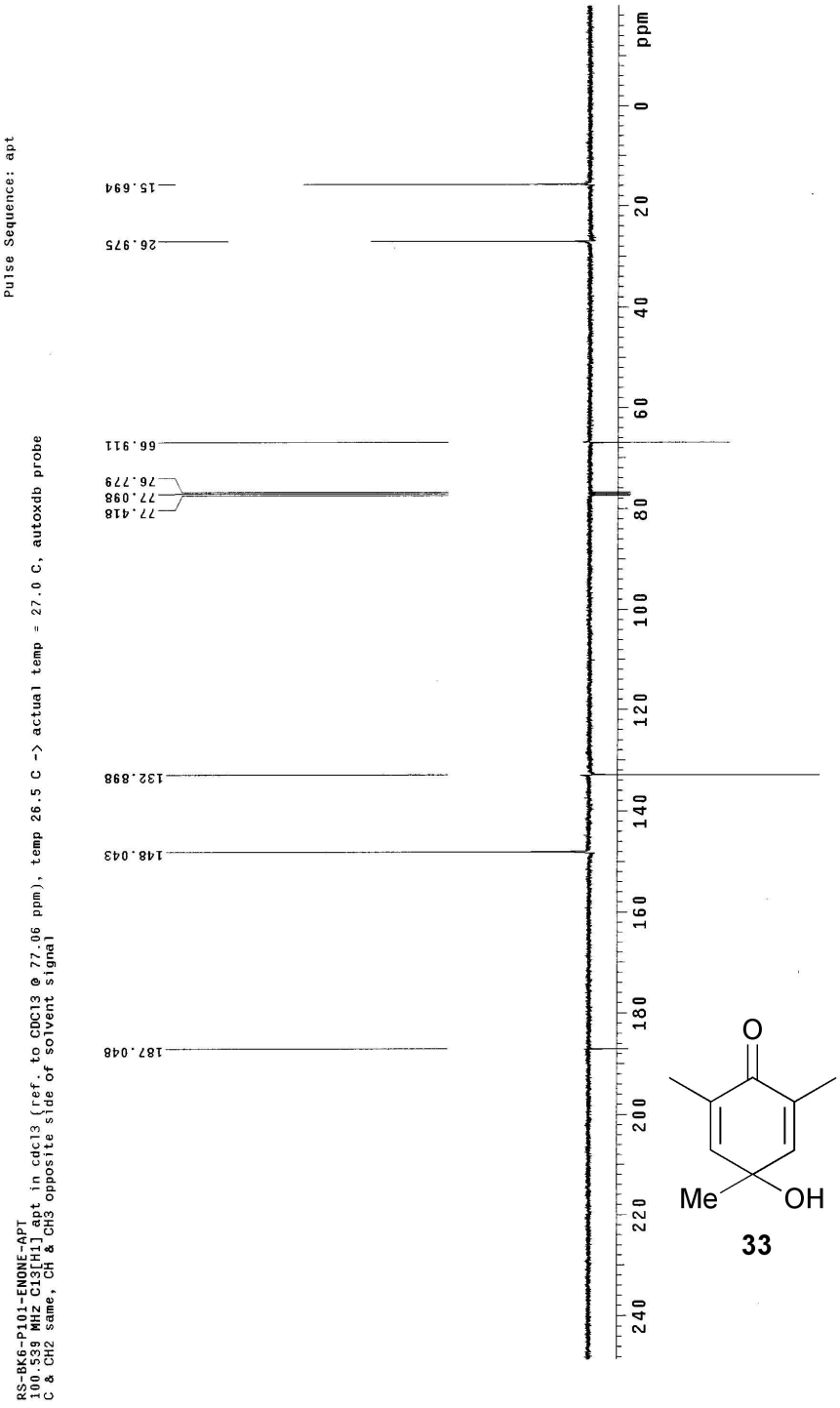

RS-BK6-P143
299.971 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.5 C -> actual temp = 27.0 C, id300 probe
Pulse Sequence: s2pul
ppm
pre-32c
Pr
OH
OAc


RS-BK6-P151-APT
125.266 MHz C13[H1] apt in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.2 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: apt
14.507
17.358
20.609
36.407
39.489
41.521
59.791
62.193
76.746
77.002
77.257
78.889
83.768
100.229
127.580
149.666
170.433
196.157
196.260
196.289
198.102
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
O
H
O
Pr
O
H
H
O
O
OAc
32c

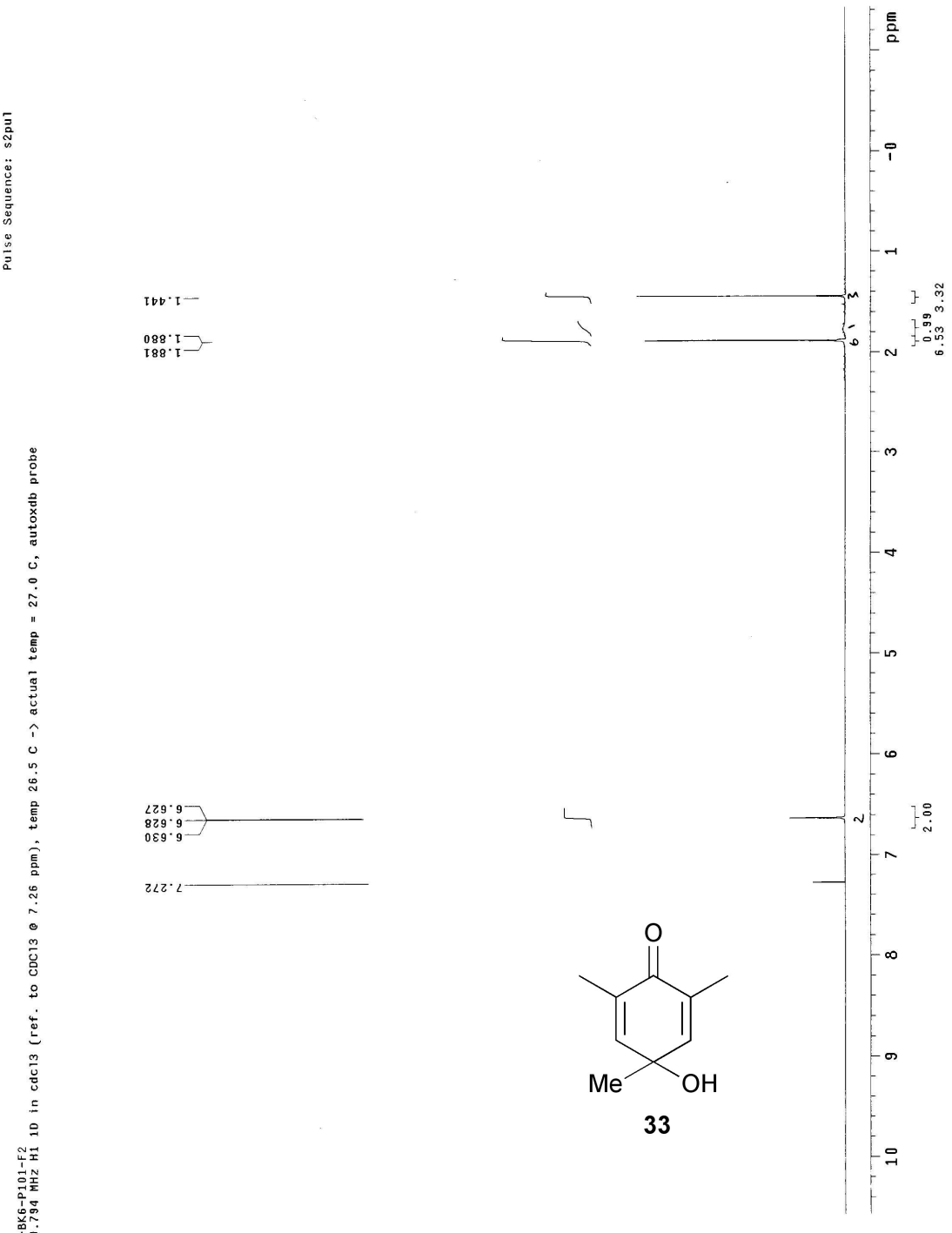

RS-BK6-P151-DP
498.122 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.2 C -> actual temp = 27.0 C, autoxdb probe
Pulse Sequence: s2pul
ppm
32c
Pr
OAc

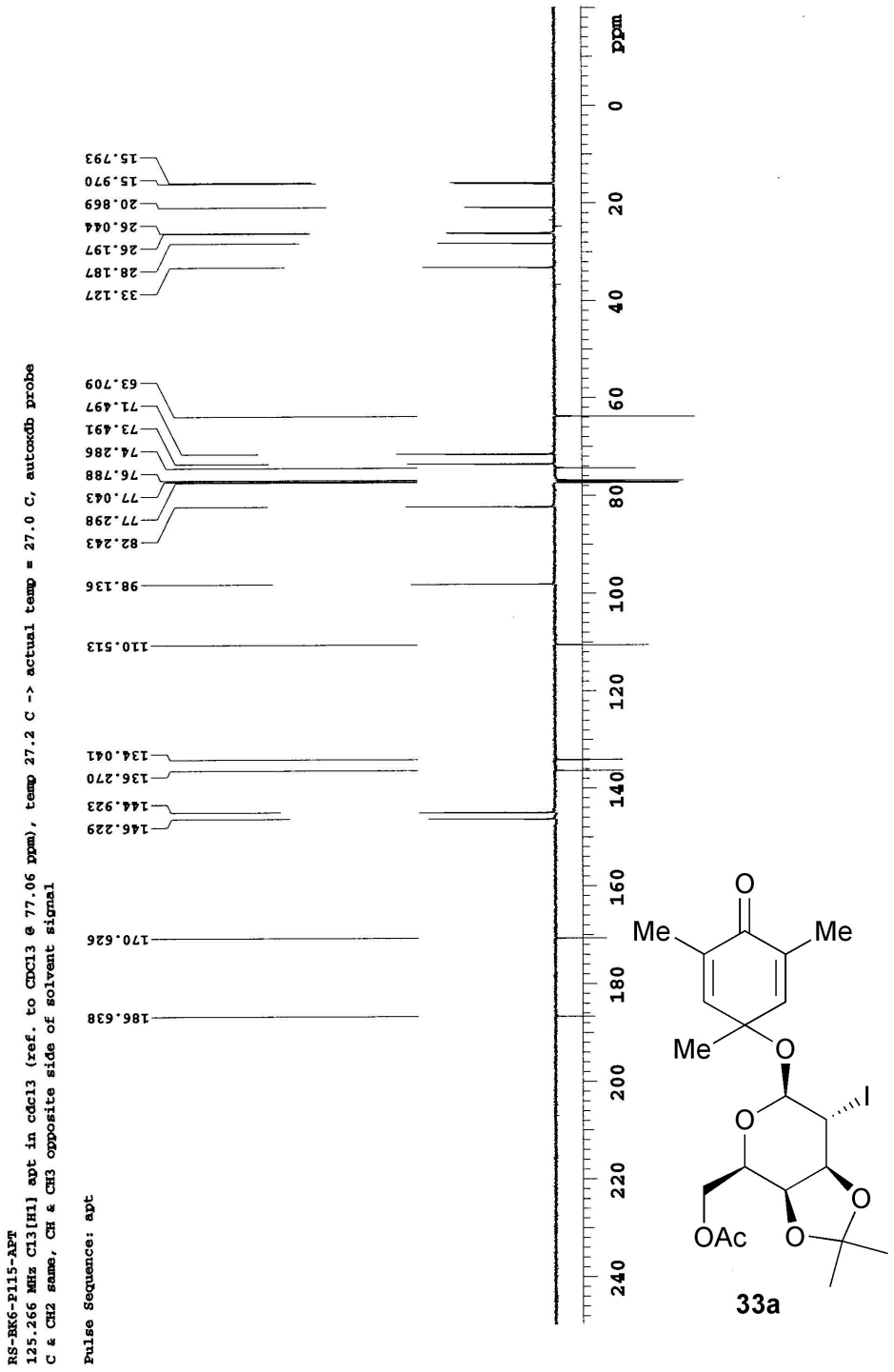

RS-BK6-PROPYL-FINAL-APT
100.539 MHz C13[H1] apt in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: apt
14.248
17.038
34.820
37.056
38.937
39.977
76.668
76.983
77.303
83.742
129.724
145.958
173.780
195.089
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
O
H
Pr
O
O
32d


RS-BK6-PROPYL-FINAL
399.794 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe
Pulse Sequence: s2pul
ppm
Pr
H
O
O
O
32d

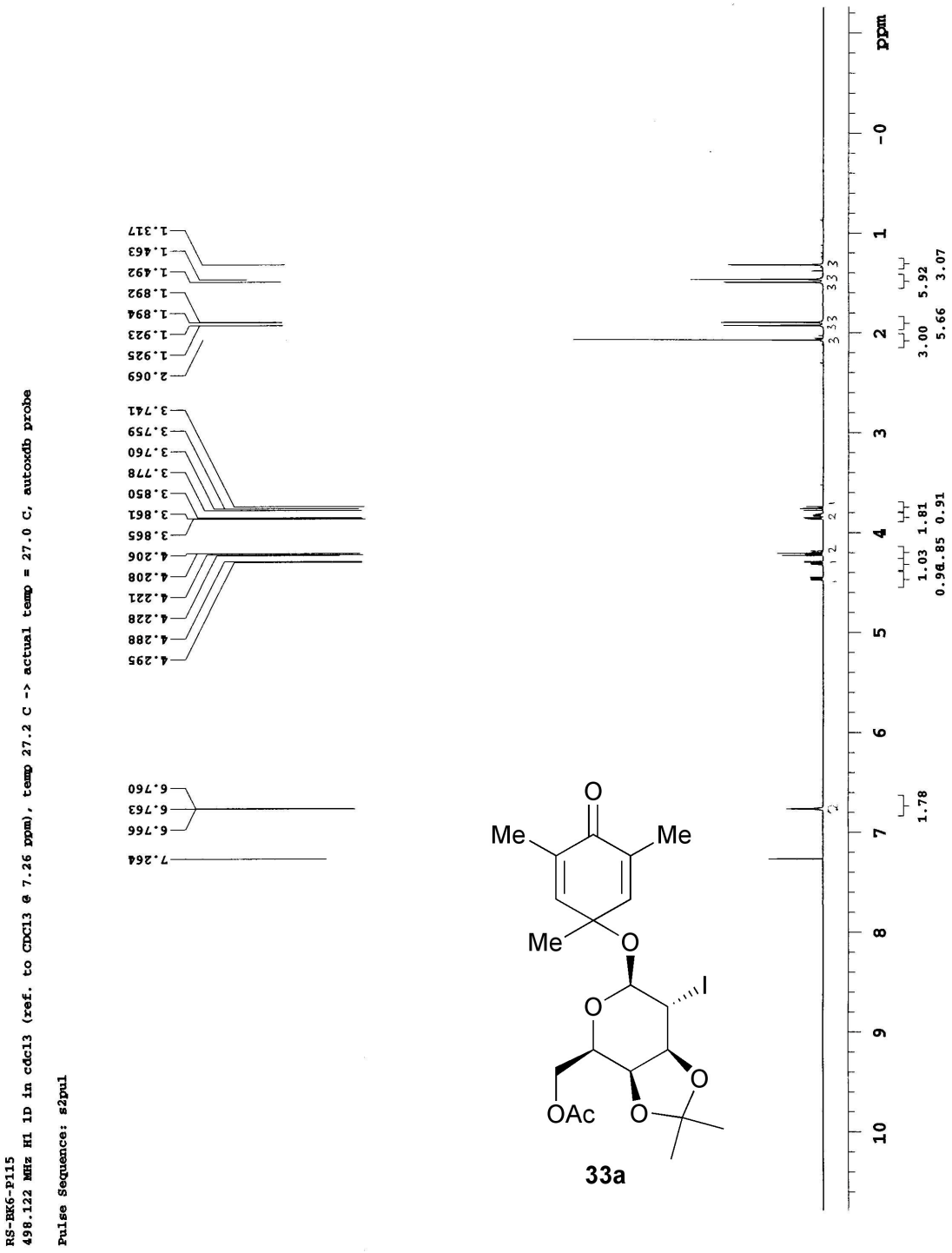

RS-BK6-P101-ENONE-APT
100.539 MHz C13[H1] apt in cdcl3 (ref. to CDC13 @ 77.06 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal)
Pulse Sequence: apt
15.694
26.975
66.911
76.779
77.098
77.418
132.898
148.043
187.048
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
O
Me
OH

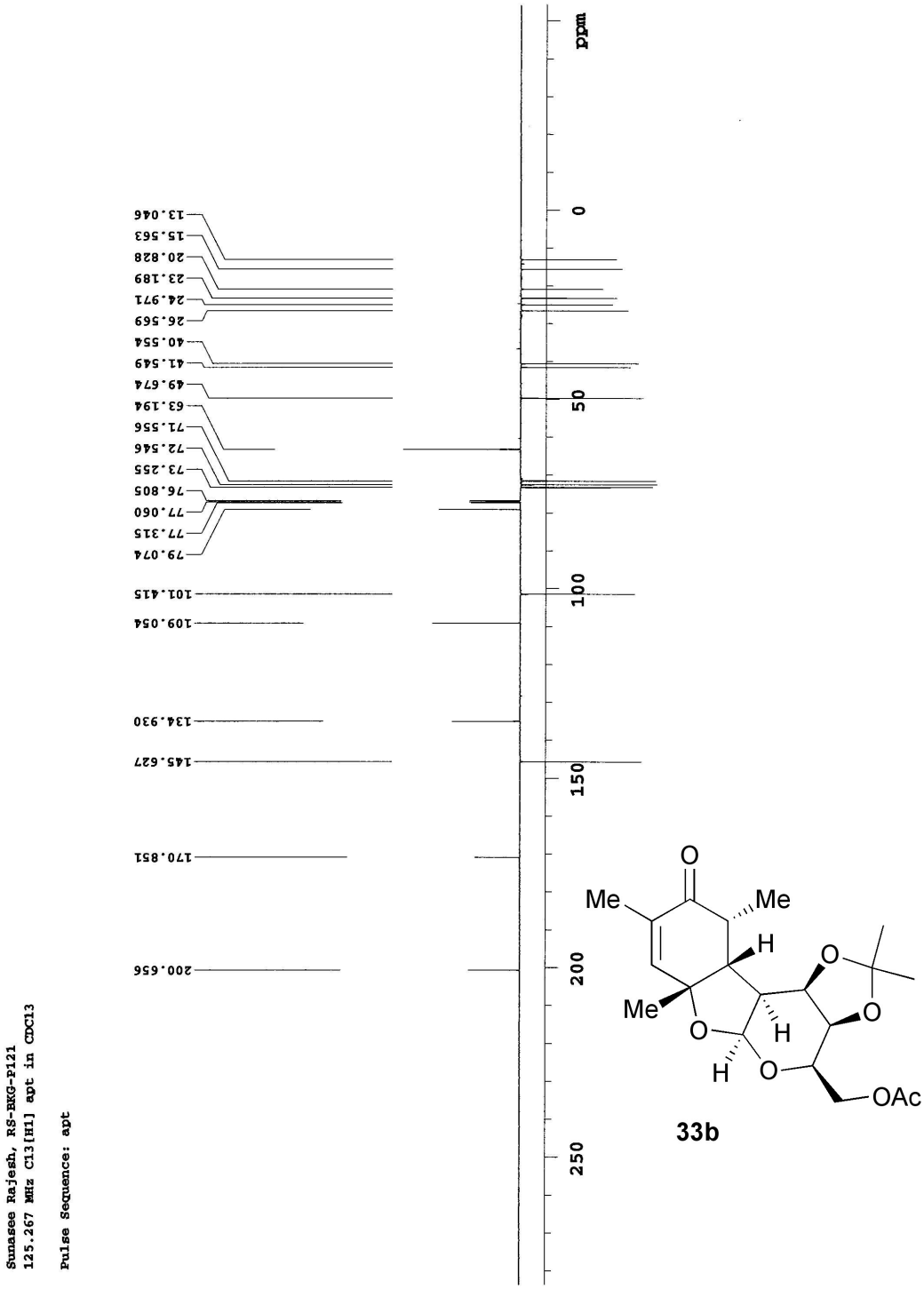
33

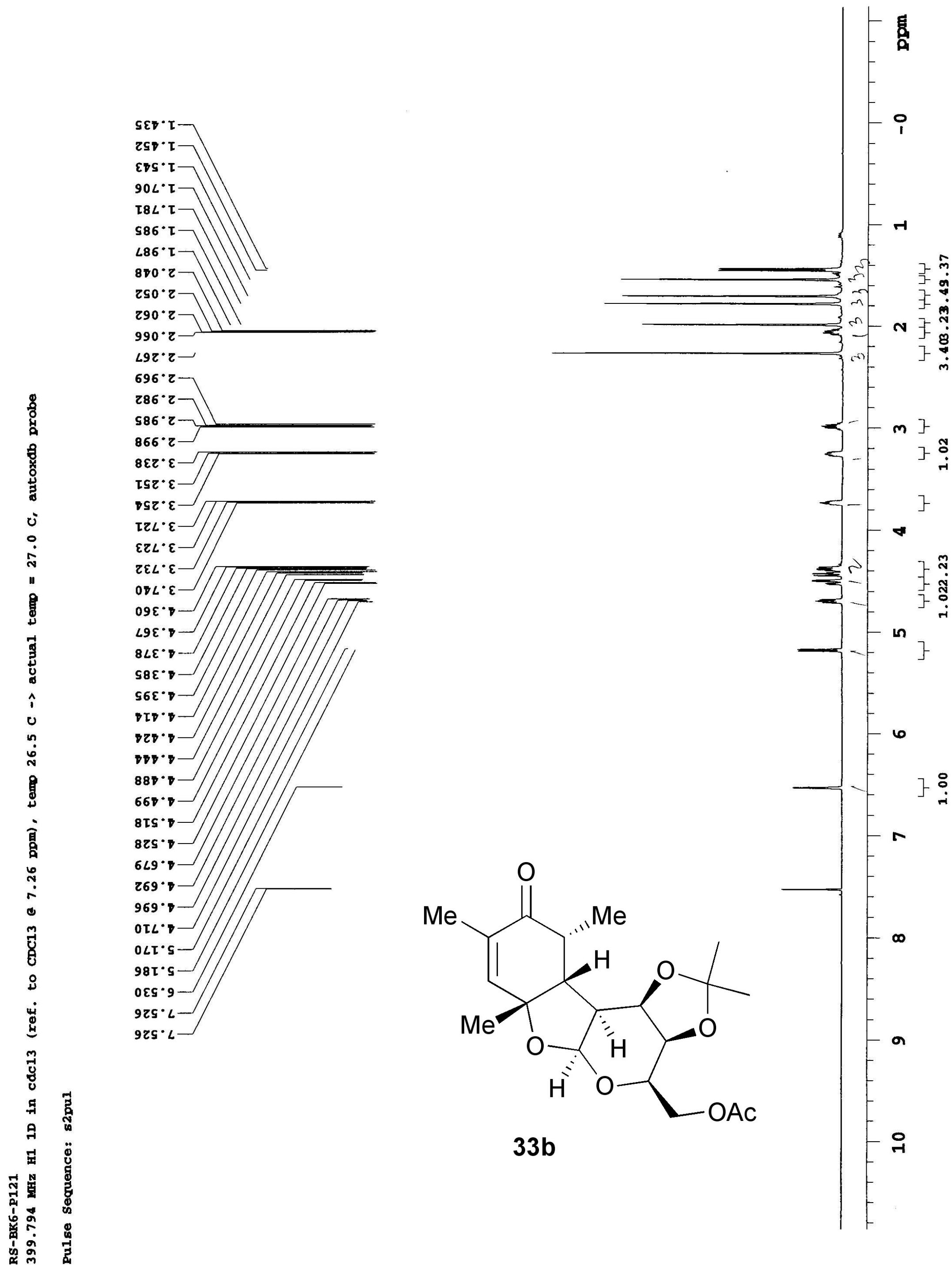

Pulse Sequence: s2pul
RS-BK6-P101-F2
399.794 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe
1.441
1.881
1.880
6.627
6.628
6.630
7.272
ppm
0.99
6.53 3.32
2.00
O
Me
OH
33

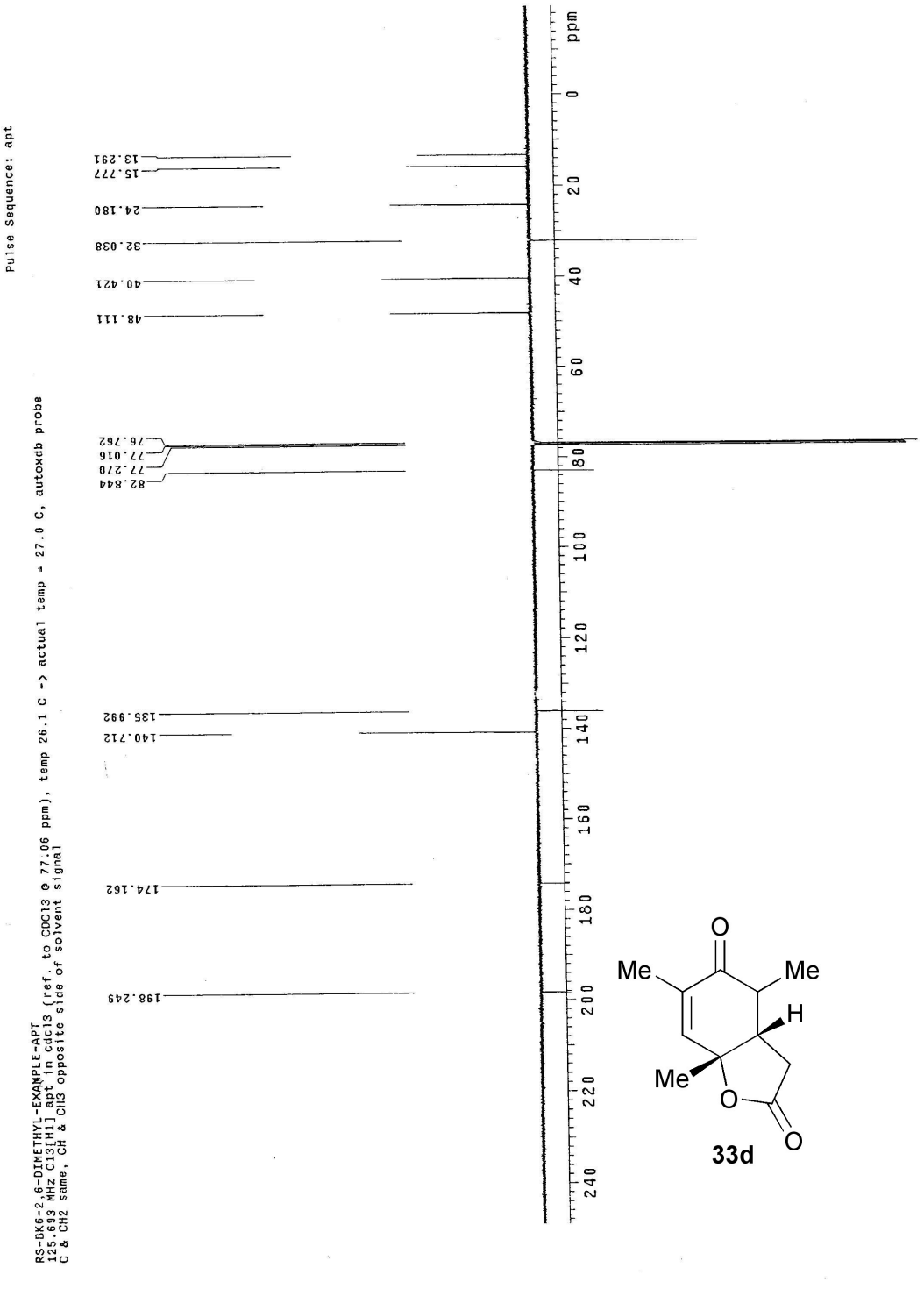

RS-BK6-P115-APT
125.266 MHz C13{H1} apt in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.2 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: apt
15.793
15.970
20.869
26.044
26.197
28.187
33.127
63.709
71.497
73.491
74.286
76.788
77.043
77.298
82.243
98.136
110.513
134.041
136.270
144.923
146.229
170.626
186.638
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
O
Me
Me
Me
O
O
I
O
O
OAc
O

33a


RS-BK6-P115
498.122 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.2 C -> actual temp = 27.0 C, autoxdb probe
Pulse Sequence: s2pul
1.317
1.463
1.492
1.892
1.894
1.923
1.925
2.069
3.741
3.759
3.760
3.778
3.850
3.861
3.865
4.206
4.208
4.221
4.228
4.288
4.295
6.760
6.763
6.766
7.264
Me
Me
Me
O
O
O
I
O
O
OAc
33a
ppm
1.78
1.03 1.81
0.98 0.85 0.91
3.00 5.92
5.66 3.07


13.046
15.563
20.828
23.189
24.971
26.569
40.554
41.549
49.674
63.194
71.556
72.546
73.255
76.805
77.060
77.315
79.074
101.415
109.054
134.930
145.627
170.851
200.656
ppm
0
50
100
150
200
250
Sunasee Rajesh, RS-RKG-P121
125.267 MHz C13[H1] apt in CDCl3
Pulse Sequence: apt
O
Me
Me
H
O
Me
O
H
O
H
O
OAc
33b

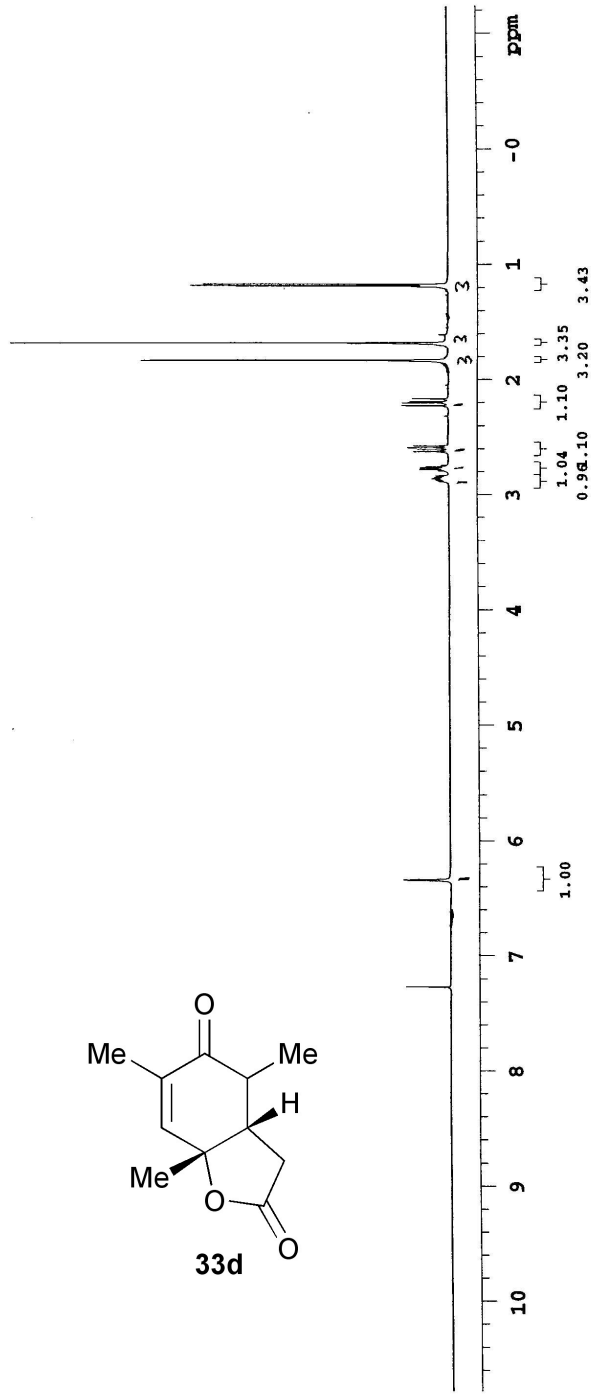

RS-BK6-P121
399.794 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe
Pulse Sequence: s2pul
ppm
Me
O
Me
H
O
O
Me
O
H
H
O
OAc
33b


Pulse Sequence: apt
RS-BK6-2,6-DIMETHYL-EXAMPLE-APT
125.693 MHz C13[H1] apt in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal
13.291
15.777
24.180
32.038
40.421
48.111
76.762
77.016
77.270
82.844
135.992
140.712
174.162
198.249
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
Me
Me
H
Me
O
O
O

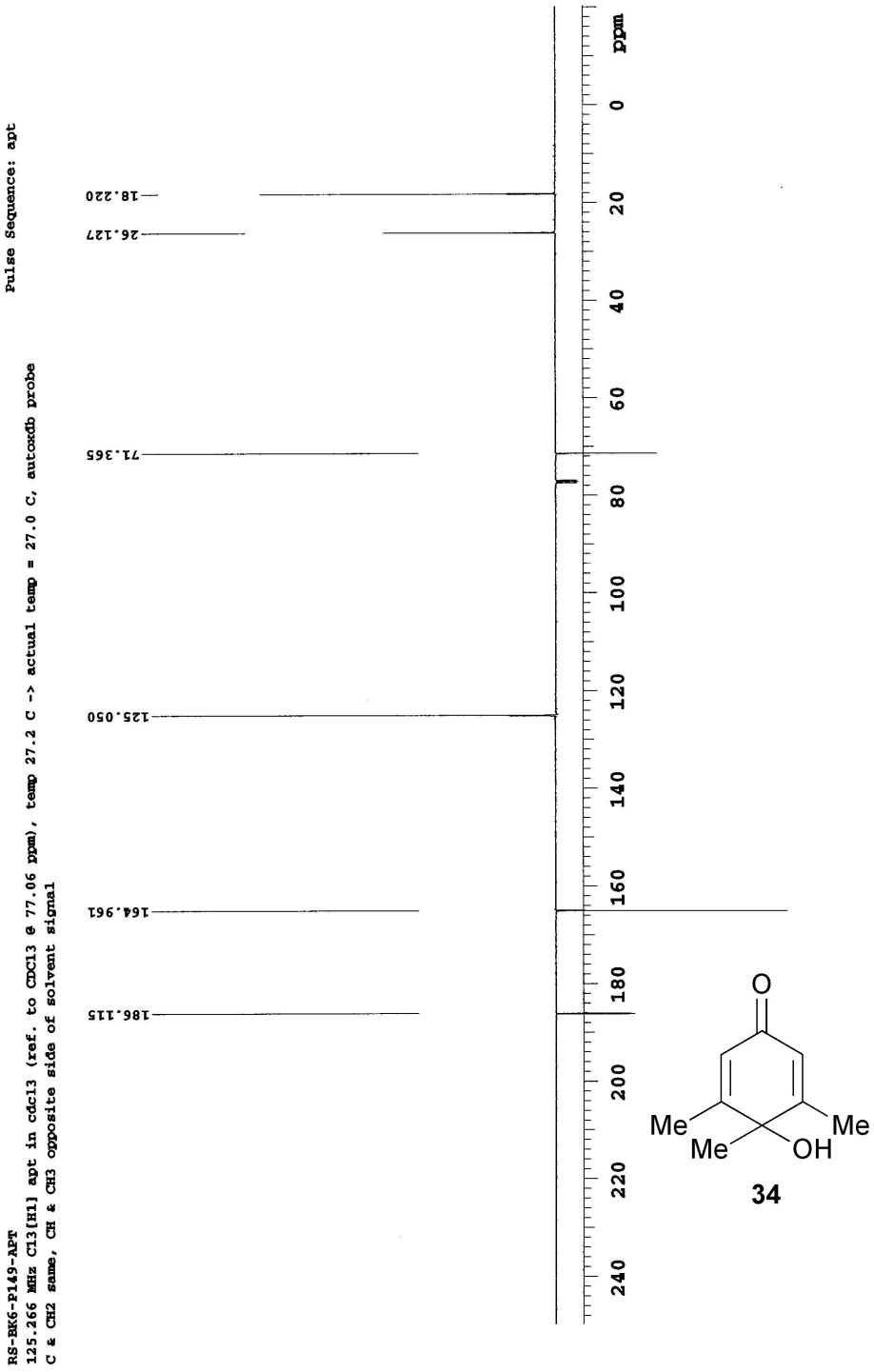
33d

RS-BK6-2,6-DIMETHYL-EXAPMLE
499.821 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxdb probe

Pulse Sequence: s2pul

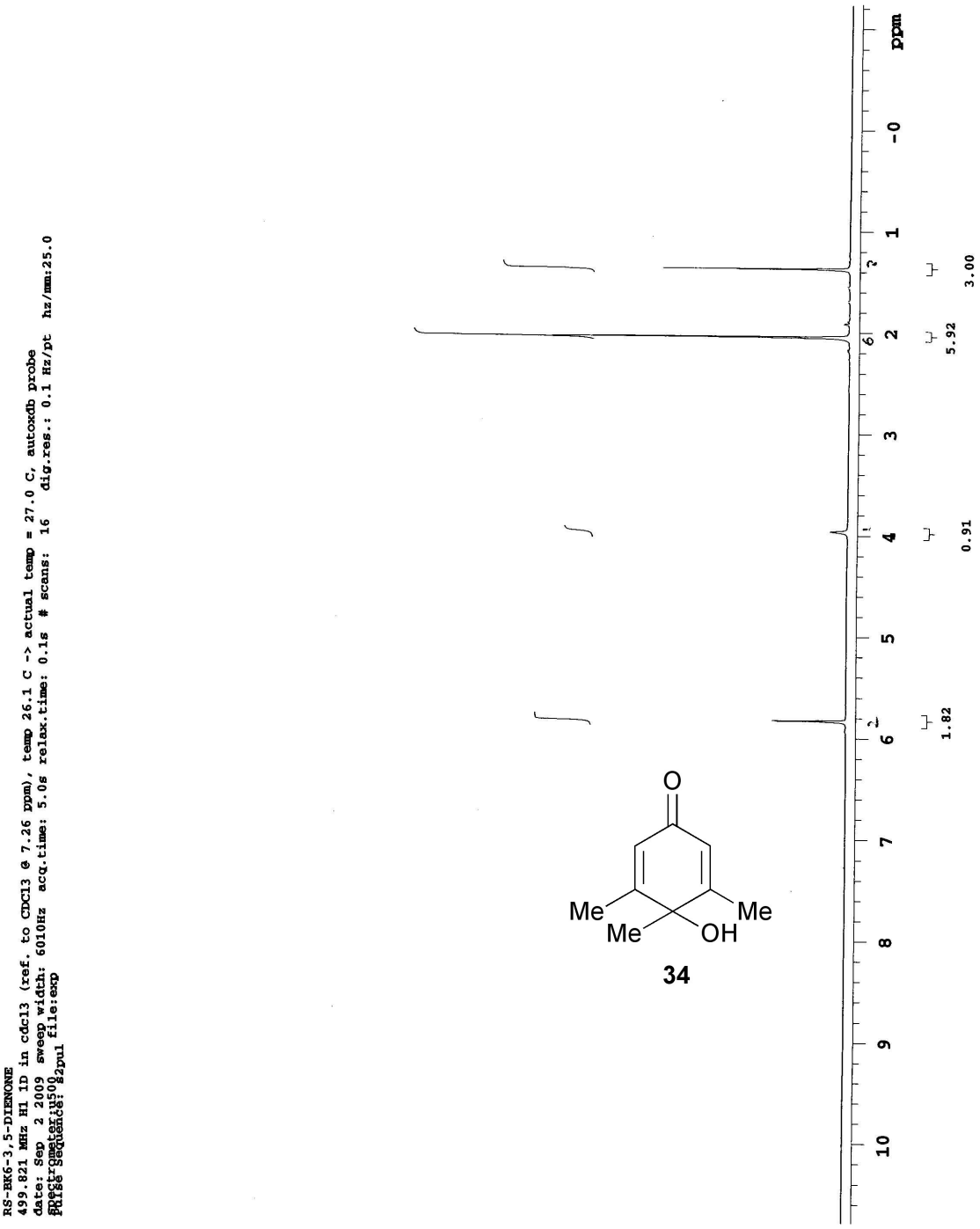


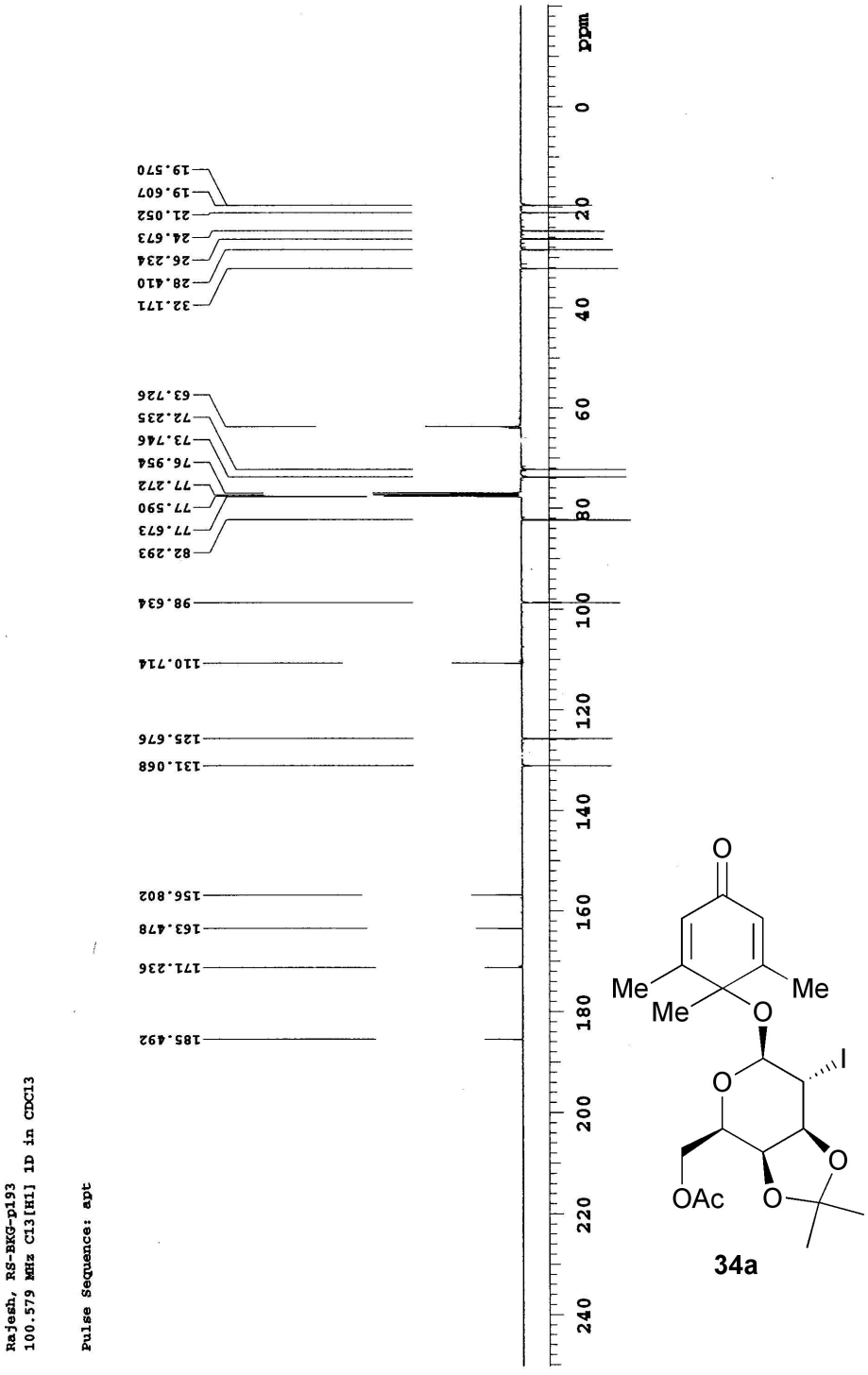
33d


RS-BK6-P149-APT
125.266 MHz C13[H1] apt in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.2 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: apt
18.220
26.127
71.365
125.050
164.961
186.115
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240

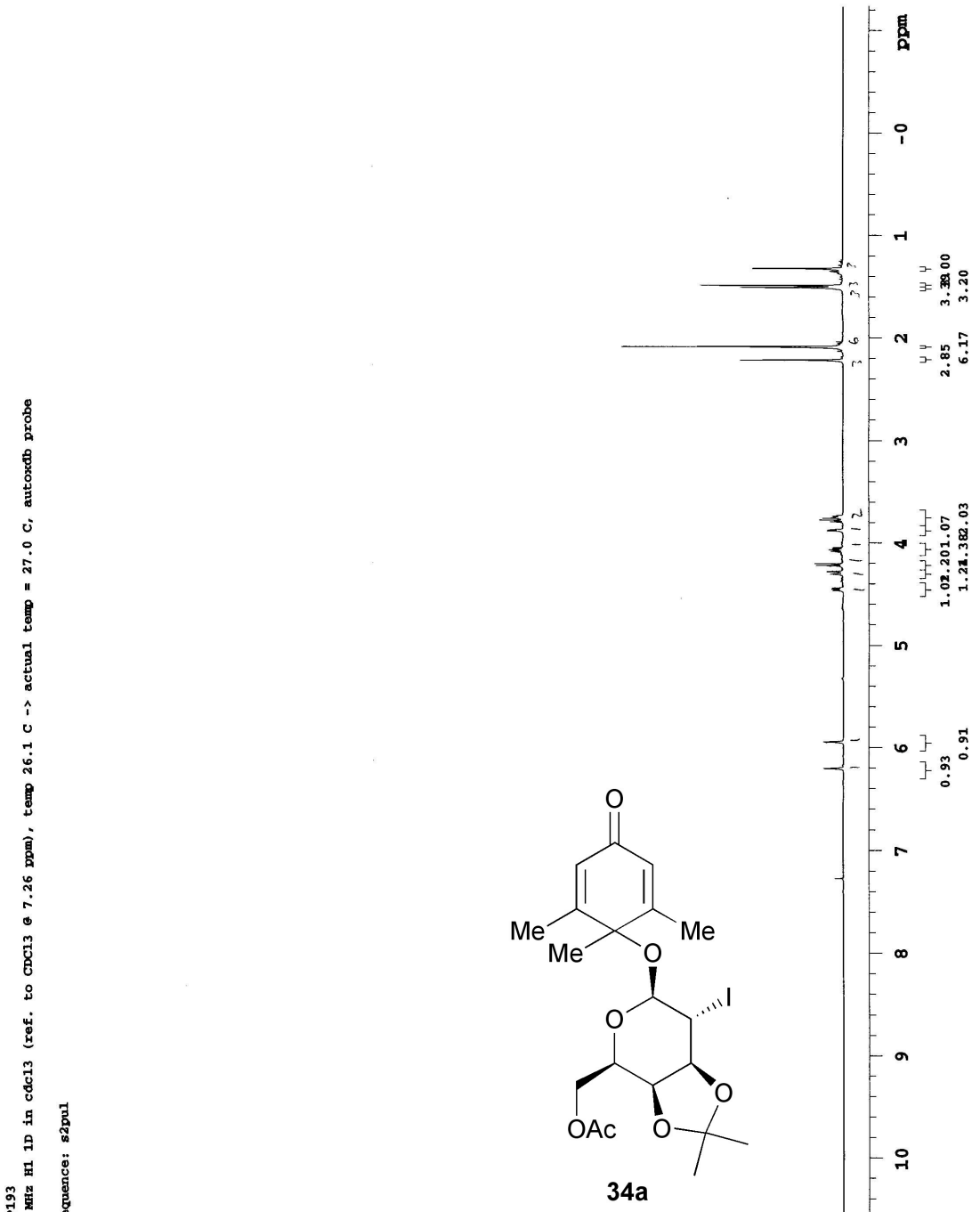
O
Me
Me
Me
OH

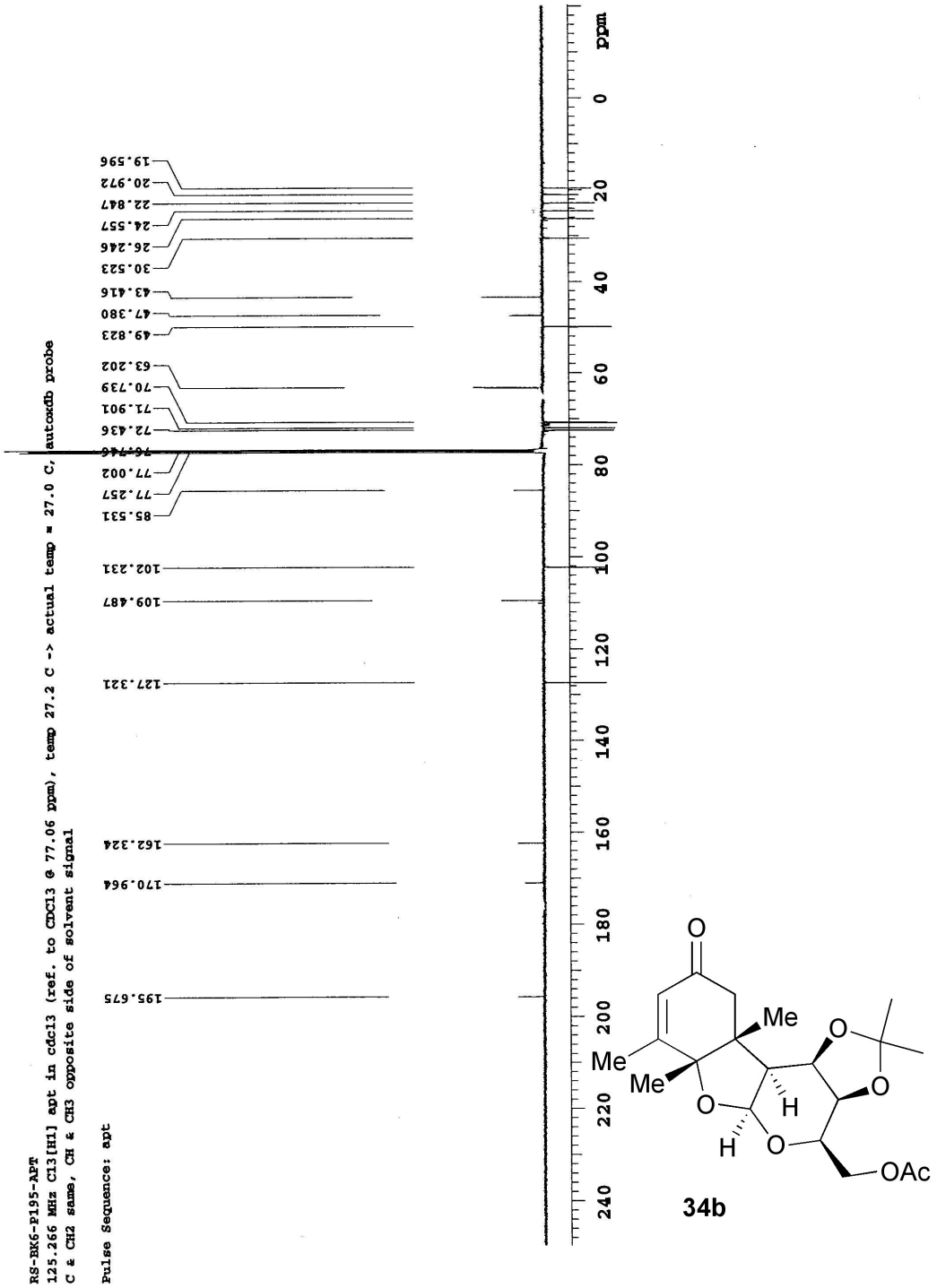
34


RS-RK6-3,5-DIENONE
499.821 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxdb probe
date: Sep 2 2009 sweep width: 6010Hz acq.time: 5.0s relax.time: 0.1s # scans: 16 dig.res.: 0.1 Hz/pt hz/mm:25.0
Pulse Sequence: s2pul file:exp
ppm
1.82
0.91
5.92
3.00
Me
Me
Me
OH
34

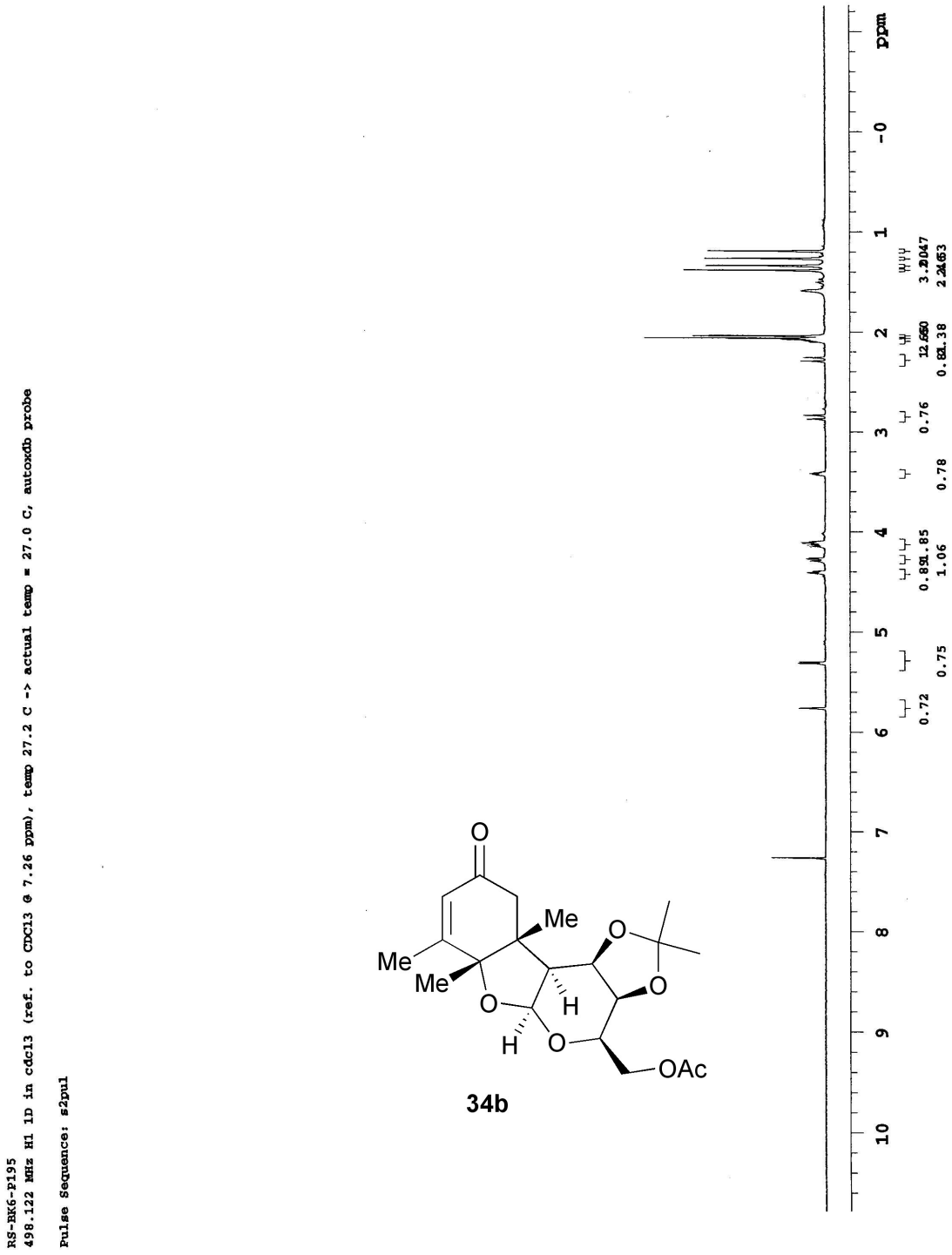

Rajesh, RS-BKG-p193
100.579 MHz C13[H1] 1D in CDCl3
Pulse Sequence: apt
19.570
19.607
21.052
24.673
26.234
28.410
32.171
63.726
72.235
73.746
76.954
77.272
77.590
77.673
82.293
98.634
110.714
125.676
131.068
156.802
163.478
171.236
185.492
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
O
Me
Me
Me
O
O
I
O
OAc
O
O

34a


RS-BK6-P193
499.821 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxdb probe
Pulse Sequence: s2pul
ppm
0.93
0.91
1.02
2.20
1.07
1.24
4.38
2.03
2.85
6.17
3.00
3.20
Me
Me
Me
O
O
O
I
O
OAc
O
34a


RS-BK6-P195-APT
125.266 MHz C13[H1] apt in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.2 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: apt
19.596
20.972
22.847
24.557
26.246
30.523
43.416
47.380
49.823
63.202
70.739
71.901
72.436
76.746
77.002
77.257
85.531
102.231
109.487
127.321
162.324
170.964
195.675
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
O
Me
Me
Me
O
O
O
H
H
O
OAc

34b

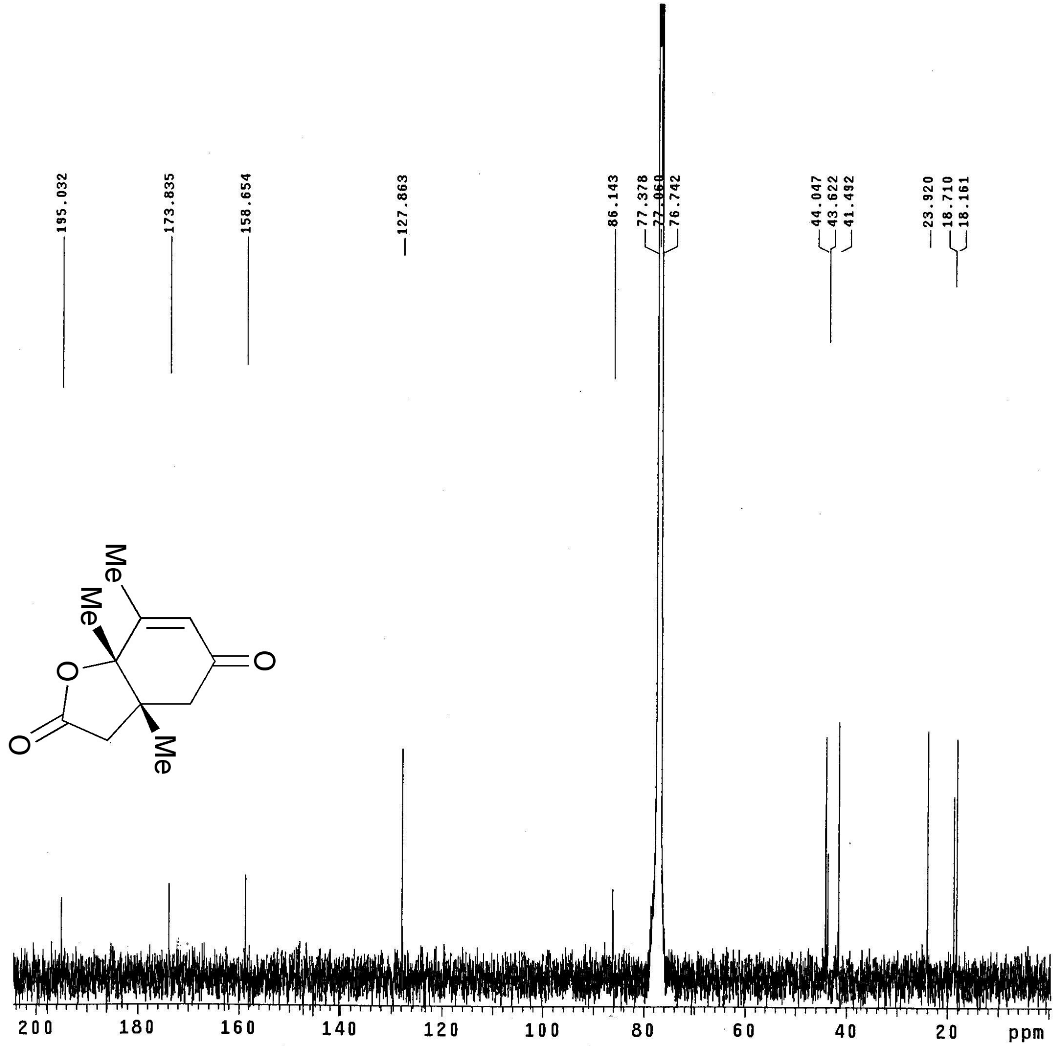

RS-BK6-P195
498.122 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.2 C -> actual temp = 27.0 C, autoxdb probe
Pulse Sequence: s2pul
ppm
0.72
0.75
0.89
1.06
1.85
0.78
0.76
12.68
0.81
1.38
3.20
47
2.24
53
O
Me
Me
Me
O
O
O
H
H
O
OAc

34b

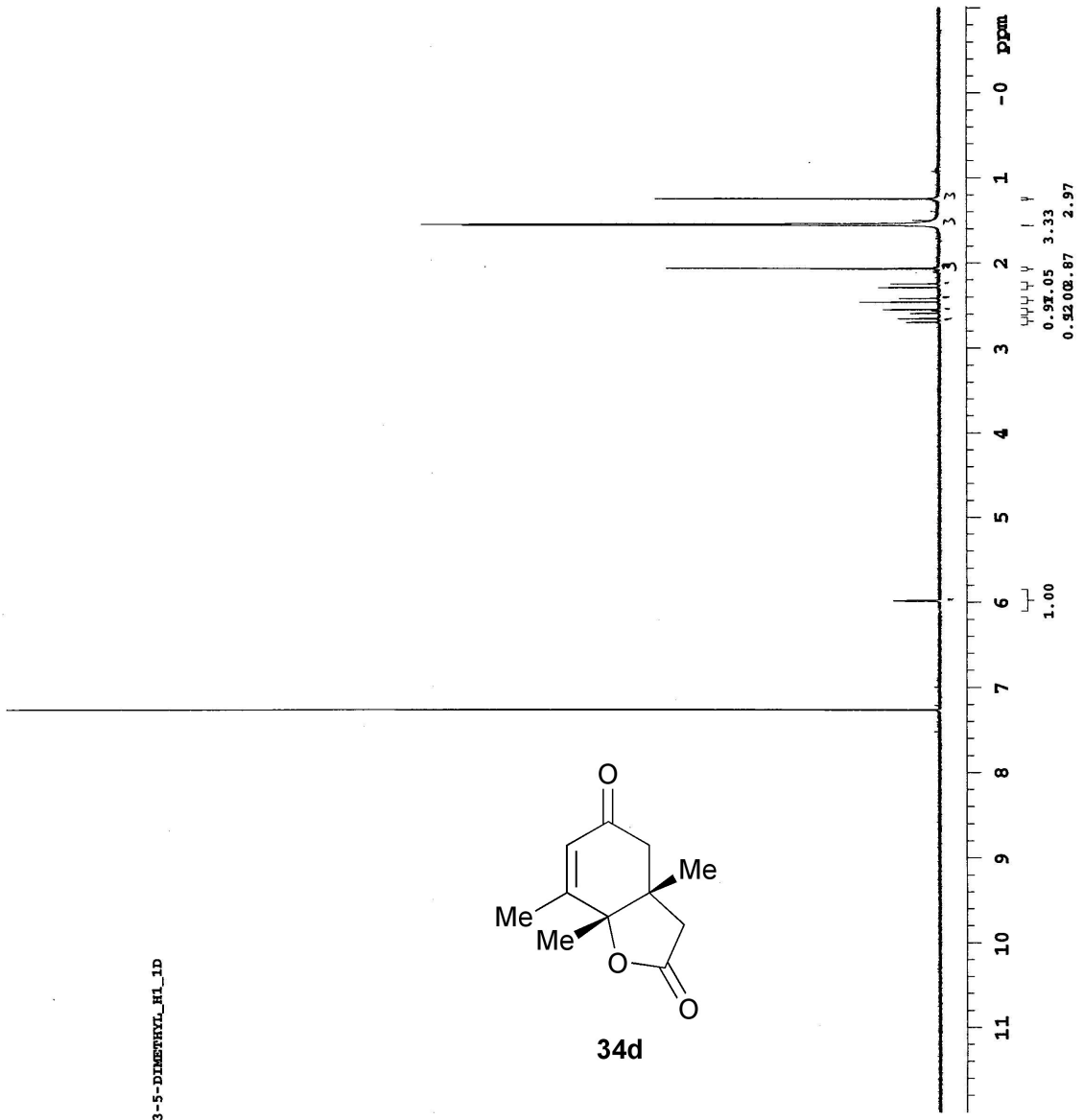
```
RS-BK6-3-5-DIMETHYL
100.579 MHz C13[H1] 1D in CDCl3

exp12  Carbon

      SAMPLE                SPECIAL
date   Sep 18 2009   temp        not used
solvent      CDCl3   gain              60
file /mnt/d600/hom~  spin        not used
e12/gennmr/nmrdata~  hst            0.008
/CLIVE/Sunasee/200~  pw90           9.300
9.09/2009.09.21.s4~  alfa          10.000
_RS-BK6-3-5-DIMETH~          FLAGS
   YL_C13_1D.fid     il                 n
   ACQUISITION       in                 n
sw         27210.9   dp                 y
at           1.992   hs                nn
np          108400        PROCESSING
fb        not used   lb              1.50
bs               4   fn          not used
ss               2         DISPLAY
d1           0.100   sp             -53.2
nt          100000   wp           20616.2
ct          100000   rfl           9807.1
   TRANSMITTER       rfp           7749.7
tn             C13   rp             -11.8
sfrq       100.579   lp            -195.9
tof         2048.7          PLOT
tpwr            55   wc               180
pw           3.100   sc                 0
   DECOUPLER         vs             55643
dn              H1   th                13
dof              0   ai  cdc  ph
dm             yyy
dmm              w
dpwr            41
dmf          10101
```



34d


Sunasee, RS-BK6-3-5-DIMETHYL
399.953 MHz H1 1D in CDCl3
(2009.09.18_4:30PM)
File: 2009.09.18.s4_RS-BK6-3-5-DIMETHYL_H1_1D
Pulse Sequence: s2pul
ppm
1.00
0.97
2.97
3.33
3.05
2.87
Me
Me
Me
O
O
O

34d

STRUCTURE REPORT

XCL Code: DLC0901 **Date:** 26 March 2009

Compound: (2,2,6a-Trimethyl-9-oxo-3a,5a,6a,9,10,10a,10b,10c-octahydro-4H-[1,3]-dioxolo[4,5]pyrano[2,3-b][1]benzofuran-4-yl)methyl acetate

Formula: $C_{18}H_{24}O_7$

Supervisor: D. L. J. Clive **Crystallographer:** R. McDonald

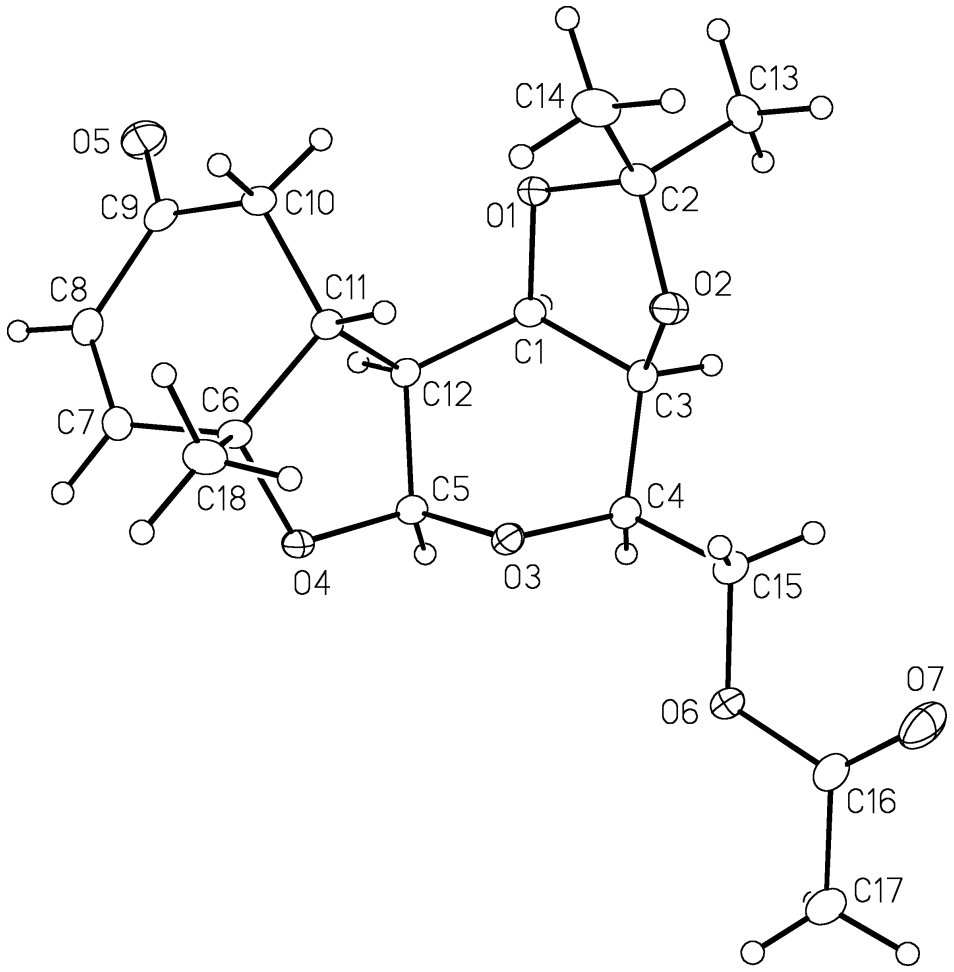
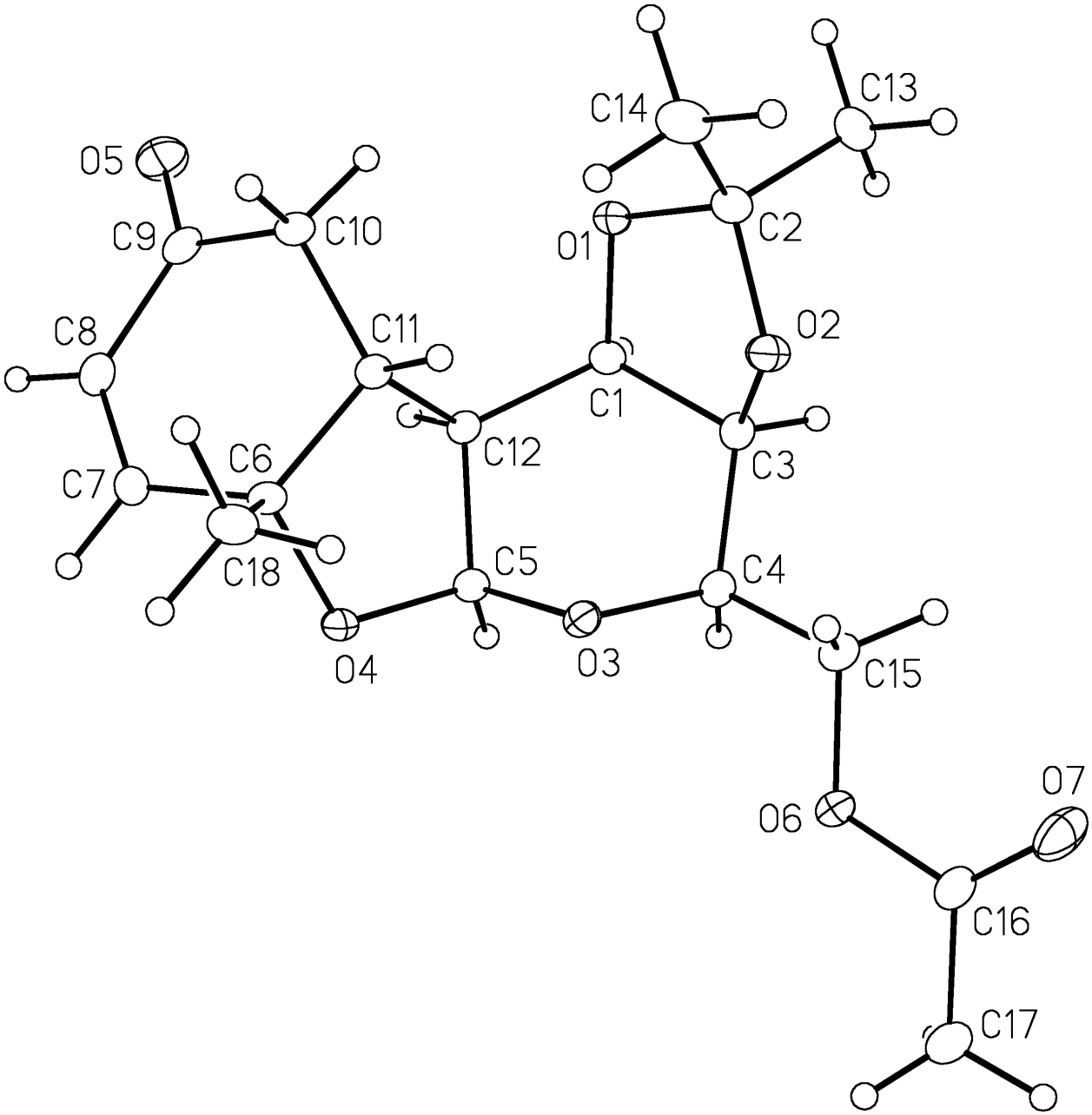
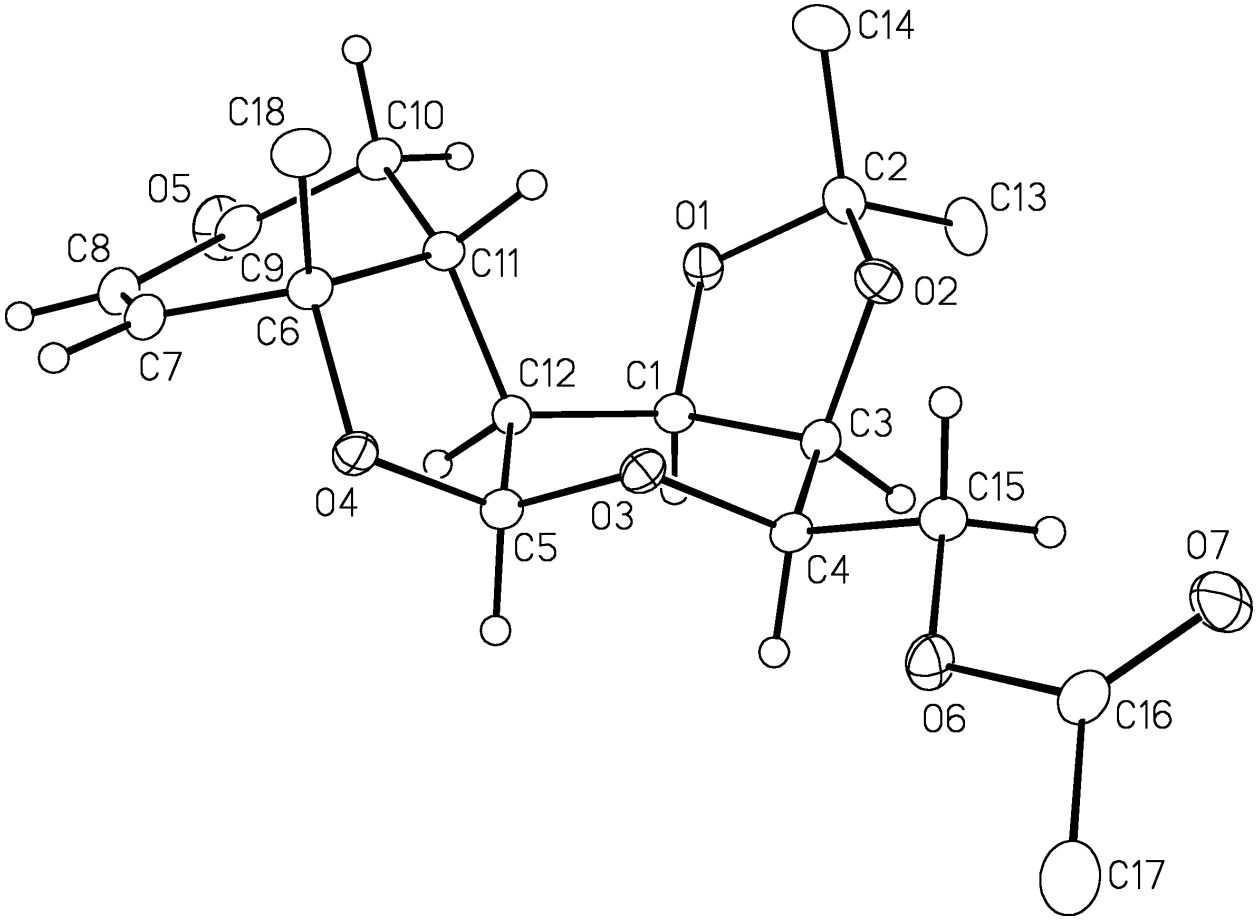


Figure Legends

Figure 1. Perspective view of the (2,2,6a-trimethyl-9-oxo-3a,5a,6a,9,10,10a,10b,10c-octahydro-4H-[1,3]dioxolo[4,5]pyrano[2,3-b][1]benzofuran-4-yl)methyl acetate molecule showing the atom labelling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters.

Figure 2. Alternate view of the molecule. Methyl hydrogens have been omitted.


C14
C13
O5
C9
C10
O1
C2
C8
C11
O2
C1
C12
C3
C7
C6
C18
C5
C4
O4
O3
C15
O7
O6
C16
C17


C14
C18
C10
C2
C13
O5
O1
C8
C9
C11
O2
C6
C7
C12
C1
C3
O4
O3
C15
C5
C4
O7
O6
C16
C17

List of Tables

Table 1. Crystallographic Experimental Details

A. Crystal Data	
formula	$C_{18}H_{24}O_7$
formula weight	352.37
crystal dimensions (mm)	0.30 × 0.24 × 0.23
crystal system	orthorhombic
space group	$P2_12_12_1$ (No. 19)
unit cell parameters[a]	
a (Å)	10.1881 (10)
b (Å)	11.5427 (12)
c (Å)	15.3396 (15)
V (Å^3)	1803.9 (3)
Z	4
ρ_{calcd} (g cm^{-3})	1.297
μ (mm^{-1})	0.100
B. Data Collection and Refinement Conditions	
diffractometer	Bruker PLATFORM/SMART 1000 CCD[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–100
scan type	ω scans (0.3°) (20 s exposures)
data collection 2θ limit (deg)	55.14
total data collected	15820 (-13 ≤ h ≤ 13, -15 ≤ k ≤ 14, -19 ≤ l ≤ 19)
independent reflections	4141 (R_{int} = 0.0376)
number of observed reflections (*NO*)	3499 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	direct methods (*SHELXS–97*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–97*[c])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.9772–0.9710
data/restraints/parameters	4141 [$F_o^2 \geq -3\sigma(F_o^2)$] / 0 / 227
Flack absolute structure parameter[d]	0.3(9)
goodness-of-fit (S)[e]	1.057 [$F_o^2 \geq -3\sigma(F_o^2)$]
final R indices[f]	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0385
wR_2 [$F_o^2 \geq -3\sigma(F_o^2)$]	0.0909
largest difference peak and hole	0.269 and –0.206 e Å^{-3}

[a]Obtained from least-squares refinement of 6200 reflections with 4.42° < 2θ < 46.32°.

[b]Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

(continued)

Table 1. Crystallographic Experimental Details (continued)

[c]Sheldrick, G. M. *Acta Crystallogr*. **2008**, *A64*, 112–122.

[d]Flack, H. D. *Acta Crystallogr*. **1983**, *A39*, 876–881; Flack, H. D.; Bernardinelli, G. *Acta Crystallogr*. **1999**, *A55*, 908–915; Flack, H. D.; Bernardinelli, G. *J. Appl. Cryst*. **2000**, *33*, 1143–1148. The Flack parameter will refine to a value near zero if the structure is in the correct configuration and will refine to a value near one for the inverted configuration. The low anomalous scattering power of the atoms in this structure (none heavier than oxygen) implies that the data cannot be used for absolute structure assignment, thus the Flack parameter is provided for informational purposes only.

[e]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0332P)^2 + 0.5280P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[f]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters

Atom	*x*	*y*	*z*	U_{eq}, Å^2
O1	0.27005(12)	0.32168(11)	0.35658(8)	0.0342(3)*
O2	0.22971(12)	0.26883(11)	0.21674(8)	0.0338(3)*
O3	0.04173(12)	0.08382(10)	0.26810(8)	0.0285(3)*
O4	0.04314(12)	-0.01985(10)	0.39362(8)	0.0314(3)*
O5	0.30190(18)	0.18374(15)	0.63385(10)	0.0597(5)*
O6	-0.10315(13)	0.10996(12)	0.10725(8)	0.0363(3)*
O7	-0.05751(16)	0.14107(17)	-0.03278(9)	0.0594(5)*
C1	0.13439(17)	0.28881(15)	0.35377(11)	0.0279(4)*
C2	0.32040(19)	0.33141(17)	0.26923(12)	0.0360(4)*
C3	0.10401(17)	0.28614(15)	0.25575(11)	0.0279(4)*
C4	0.01078(17)	0.19157(14)	0.22740(11)	0.0278(4)*
C5	0.01744(17)	0.09010(14)	0.35920(11)	0.0273(4)*
C6	0.17600(17)	-0.02463(15)	0.42934(12)	0.0294(4)*
C7	0.15561(19)	-0.05230(16)	0.52433(12)	0.0339(4)*
C8	0.19863(19)	0.01176(17)	0.59005(12)	0.0368(4)*
C9	0.2779(2)	0.11640(18)	0.57539(12)	0.0377(4)*
C10	0.33091(18)	0.13165(17)	0.48468(12)	0.0351(4)*
C11	0.23417(17)	0.09604(14)	0.41338(11)	0.0268(4)*
C12	0.11313(17)	0.17387(15)	0.40357(11)	0.0259(4)*
C13	0.3270(2)	0.45828(17)	0.24385(13)	0.0454(5)*
C14	0.4520(2)	0.2719(2)	0.26304(16)	0.0502(6)*
C15	0.01401(17)	0.17368(17)	0.13029(11)	0.0312(4)*
C16	-0.12958(19)	0.10283(17)	0.02169(12)	0.0349(4)*
C17	-0.2590(3)	0.0481(2)	0.00427(15)	0.0590(7)*
C18	0.2532(2)	-0.11850(16)	0.38288(14)	0.0391(5)*

Anisotropically-refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$.

Table 3. Selected Interatomic Distances (Å)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
O1	C1	1.434(2)	C2	C13	1.517(3)
O1	C2	1.439(2)	C2	C14	1.509(3)
O2	C2	1.423(2)	C3	C4	1.511(2)
O2	C3	1.428(2)	C4	C15	1.504(2)
O3	C4	1.427(2)	C5	C12	1.533(2)
O3	C5	1.421(2)	C6	C7	1.506(3)
O4	C5	1.399(2)	C6	C11	1.533(2)
O4	C6	1.461(2)	C6	C18	1.517(3)
O5	C9	1.212(2)	C7	C8	1.325(3)
O6	C15	1.446(2)	C8	C9	1.470(3)
O6	C16	1.342(2)	C9	C10	1.503(3)
O7	C16	1.197(2)	C10	C11	1.529(2)
C1	C3	1.535(2)	C11	C12	1.533(2)
C1	C12	1.546(2)	C16	C17	1.486(3

Table 4. Selected Interatomic Angles (deg)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C1	O1	C2	109.65(13)	O4	C6	C7	104.07(14)
C2	O2	C3	105.92(13)	O4	C6	C11	105.30(13)
C4	O3	C5	110.32(12)	O4	C6	C18	109.35(14)
C5	O4	C6	110.43(12)	C7	C6	C11	113.61(15)
C15	O6	C16	115.84(14)	C7	C6	C18	112.00(16)
O1	C1	C3	103.24(14)	C11	C6	C18	111.92(15)
O1	C1	C12	110.32(14)	C6	C7	C8	124.90(17)
C3	C1	C12	116.00(14)	C7	C8	C9	121.59(18)
O1	C2	O2	104.82(14)	O5	C9	C8	121.64(19)
O1	C2	C13	109.28(16)	O5	C9	C10	122.52(19)
O1	C2	C14	109.86(16)	C8	C9	C10	115.80(16)
O2	C2	C13	111.95(16)	C9	C10	C11	113.53(15)
O2	C2	C14	108.08(16)	C6	C11	C10	112.29(14)
C13	C2	C14	112.55(18)	C6	C11	C12	103.71(13)
O2	C3	C1	103.45(14)	C10	C11	C12	115.55(14)
O2	C3	C4	110.01(14)	C1	C12	C5	114.27(14)
C1	C3	C4	115.03(14)	C1	C12	C11	116.02(14)
O3	C4	C3	111.40(13)	C5	C12	C11	100.69(13)
O3	C4	C15	107.99(14)	O6	C15	C4	107.09(14)
C3	C4	C15	111.74(14)	O6	C16	O7	122.48(18)
O3	C5	O4	106.99(13)	O6	C16	C17	112.33(17)
O3	C5	C12	110.99(13)	O7	C16	C17	125.14(18)
O4	C5	C12	106.59(13)				

Table 5. Torsional Angles (deg)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
C2	O1	C1	C3	-3.16(17)	O2	C3	C4	O3	72.60(17)
C2	O1	C1	C12	121.40(15)	O2	C3	C4	C15	-48.29(19)
C1	O1	C2	O2	-18.49(18)	C1	C3	C4	O3	-43.7(2)
C1	O1	C2	C13	101.66(18)	C1	C3	C4	C15	-164.60(15)
C1	O1	C2	C14	-134.40(16)	O3	C4	C15	O6	74.38(17)
C3	O2	C2	O1	34.15(18)	C3	C4	C15	O6	-162.76(14)
C3	O2	C2	C13	-84.20(18)	O3	C5	C12	C1	43.86(19)
C3	O2	C2	C14	151.28(15)	O3	C5	C12	C11	-81.23(15)
C2	O2	C3	C1	-35.74(18)	O4	C5	C12	C1	160.02(14)
C2	O2	C3	C4	-159.11(14)	O4	C5	C12	C11	34.93(16)
C5	O3	C4	C3	67.29(17)	O4	C6	C7	C8	-122.86(19)
C5	O3	C4	C15	-169.65(13)	C11	C6	C7	C8	-8.9(3)
C4	O3	C5	O4	176.90(13)	C18	C6	C7	C8	119.1(2)
C4	O3	C5	C12	-67.19(17)	O4	C6	C11	C10	147.81(15)
C6	O4	C5	O3	96.63(15)	O4	C6	C11	C12	22.38(17)
C6	O4	C5	C12	-22.17(18)	C7	C6	C11	C10	34.6(2)
C5	O4	C6	C7	119.44(15)	C7	C6	C11	C12	-90.86(17)
C5	O4	C6	C11	-0.33(18)	C18	C6	C11	C10	-93.48(18)
C5	O4	C6	C18	-120.74(15)	C18	C6	C11	C12	141.08(15)
C16	O6	C15	C4	168.91(15)	C6	C7	C8	C9	-2.9(3)
C15	O6	C16	O7	3.9(3)	C7	C8	C9	O5	169.6(2)
C15	O6	C16	C17	-173.35(18)	C7	C8	C9	C10	-12.7(3)
O1	C1	C3	O2	23.49(17)	O5	C9	C10	C11	-143.01(19)
O1	C1	C3	C4	143.49(14)	C8	C9	C10	C11	39.2(2)
C12	C1	C3	O2	-97.28(17)	C9	C10	C11	C6	-50.1(2)
C12	C1	C3	C4	22.7(2)	C9	C10	C11	C12	68.6(2)
O1	C1	C12	C5	-139.57(14)	C6	C11	C12	C1	-157.82(14)
O1	C1	C12	C11	-23.0(2)	C6	C11	C12	C5	-33.93(16)
C3	C1	C12	C5	-22.7(2)	C10	C11	C12	C1	78.85(19)
C3	C1	C12	C11	93.85(18)	C10	C11	C12	C5	-157.25(14)

Table 6. Anisotropic Displacement Parameters (U_{ij}, Å^2)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	0.0352(7)	0.0374(7)	0.0300(6)	0.0032(5)	-0.0051(5)	-0.0122(6)
O2	0.0309(7)	0.0384(7)	0.0323(6)	-0.0052(5)	0.0022(5)	-0.0061(6)
O3	0.0296(6)	0.0276(6)	0.0282(6)	-0.0023(5)	-0.0045(5)	0.0019(5)
O4	0.0264(6)	0.0292(6)	0.0385(7)	0.0043(5)	-0.0076(6)	-0.0056(5)
O5	0.0762(12)	0.0598(10)	0.0432(8)	-0.0114(8)	-0.0158(8)	-0.0183(9)
O6	0.0400(7)	0.0406(7)	0.0284(7)	0.0004(6)	-0.0080(6)	-0.0098(6)
O7	0.0422(8)	0.1071(14)	0.0288(7)	-0.0084(8)	0.0011(7)	-0.0087(9)
C1	0.0280(9)	0.0261(8)	0.0294(9)	-0.0025(7)	-0.0014(7)	-0.0009(7)
C2	0.0357(10)	0.0396(10)	0.0326(9)	0.0003(8)	-0.0004(8)	-0.0094(9)
C3	0.0310(9)	0.0257(8)	0.0271(9)	-0.0001(7)	-0.0013(7)	0.0023(7)
C4	0.0255(8)	0.0298(9)	0.0282(9)	0.0007(7)	-0.0018(7)	0.0036(7)
C5	0.0256(9)	0.0271(8)	0.0293(9)	-0.0007(7)	-0.0025(7)	-0.0006(7)
C6	0.0256(9)	0.0275(8)	0.0349(9)	-0.0008(8)	-0.0056(7)	-0.0031(7)
C7	0.0323(10)	0.0317(9)	0.0378(10)	0.0084(8)	-0.0045(8)	-0.0014(8)
C8	0.0392(11)	0.0404(11)	0.0309(9)	0.0055(8)	-0.0048(8)	0.0022(9)
C9	0.0367(10)	0.0399(10)	0.0365(10)	-0.0004(9)	-0.0151(9)	0.0000(9)
C10	0.0276(9)	0.0339(10)	0.0439(11)	0.0038(8)	-0.0096(8)	-0.0049(8)
C11	0.0248(8)	0.0285(8)	0.0272(8)	-0.0013(7)	-0.0013(7)	-0.0007(7)
C12	0.0257(8)	0.0292(8)	0.0227(8)	-0.0008(7)	-0.0017(7)	-0.0016(7)
C13	0.0584(13)	0.0401(11)	0.0376(11)	0.0045(9)	0.0011(10)	-0.0167(10)
C14	0.0324(11)	0.0573(13)	0.0609(15)	0.0019(11)	0.0030(10)	-0.0078(10)
C15	0.0280(9)	0.0375(9)	0.0280(9)	-0.0038(8)	-0.0020(7)	0.0004(8)
C16	0.0374(10)	0.0378(10)	0.0294(10)	-0.0034(8)	-0.0063(8)	0.0054(9)
C17	0.0629(15)	0.0745(16)	0.0397(11)	0.0057(11)	-0.0173(11)	-0.0275(14)
C18	0.0338(10)	0.0309(9)	0.0527(12)	-0.0073(9)	-0.0032(9)	-0.0001(9)

The form of the anisotropic displacement parameter is:
$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$

Table 7. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms

Atom	*x*	*y*	*z*	U_{eq}, Å^2
H1	0.0806	0.3509	0.3818	0.033
H3	0.0684	0.3631	0.2373	0.034
H4	-0.0803	0.2143	0.2446	0.033
H5	-0.0755	0.1134	0.3708	0.033
H7	0.1084	-0.1208	0.5382	0.041
H8	0.1777	-0.0104	0.6481	0.044
H10A	0.4119	0.0849	0.4786	0.042
H10B	0.3549	0.2140	0.4762	0.042
H11	0.2820	0.0948	0.3565	0.032
H12	0.0788	0.1923	0.4630	0.031
H13A	0.2396	0.4929	0.2489	0.054
H13B	0.3578	0.4650	0.1835	0.054
H13C	0.3880	0.4988	0.2827	0.054
H14A	0.4427	0.1905	0.2801	0.060
H14B	0.5145	0.3103	0.3021	0.060
H14C	0.4843	0.2764	0.2030	0.060
H15A	0.0157	0.2493	0.0998	0.037
H15B	0.0933	0.1294	0.1135	0.037
H17A	-0.2771	0.0501	-0.0585	0.071
H17B	-0.3277	0.0906	0.0355	0.071
H17C	-0.2575	-0.0325	0.0243	0.071
H18A	0.2132	-0.1941	0.3946	0.047
H18B	0.3440	-0.1184	0.4040	0.047
H18C	0.2525	-0.1036	0.3200	0.047